SYNTHESIS, SPECTROSCOPIC CHARACTERISATION, AND KINETIC PARAMETER STUDY OF LABILE CHROMIUM COMPLEXES USING BENZOIC ACID AS A LIGAND

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ABSTRACT

Ethanol was used as the solvent in the process of producing chromium benzoic acid complexes by combining CrO_3 (chromium trioxide) and benzoic acid. Its spectrum characteristics were evaluated by the use of elemental analysis, FAB-Mass Spectroscopy,[1] HNMR spectroscopy, FTIR Spectroscopy, UV-Vis Spectroscopy, and ICP-OES, and its thermal decomposition has been studied through DSC. The Objective was to get inside of thermal stability, the heat of energy, and the rate of decomposition of the complexes. The kinetic parameter, low amount of activation energy, and enthalpy of reaction, all pointed to the complexes having a high degree of liability.

Keywords: Chromium Complexes, Decomposition, Kinetics, Lability.

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INTRODUCTION

It is generally known that chromium (VI) is a carcinogen as well as a mutagen, but it is also effective to minimize it to a lower oxidation state using a broad range of organic reductants. As good complexing agents for hypervalent chrome as salicylic acid or other ligands with two oxygens, these ligands have the capacity to create five-membered rings around the metal ion, which may help stabilize chrome's oxidation states. Salicylic acid is one example of such a ligand.[1] Cr (III) complexes' reactivity is characterized by very slow ligand substitution processes, which results in exceptional configurational stability.[2] Under some conditions, chromium ligand substitution reactions have the potential to proceed quickly and might offer a mechanism for the process.[3] Many additional systems, including Cr (EDTA) (H_2O) and porphyrin complexes, show comparable kinetic behavior to the Cr (III)-Schiff's bases combination with nicotinic acid. In the Thermal analysis approaches DSC (differential scanning calorimetry) is of particular importance. The simplicity with which samples may be prepared for DSC analysis sets it apart from competing methods. Furthermore, the activation conditions are simply adjustable. There are several advantages to using the DSC method for thermodynamic and kinetic measurements concurrently. The DSC technique may be used for all reactions since practically all processes generate or consume heat.[4] Chromium (III) was shown to have an important role in maintaining proper glucose, lipid, and protein metabolism in humans.[5] The production of a chromium (III)-organic acid complex is an exciting area of research because of the compounds' involvement in the hazardous Cr (VI) being reduced to Cr (III)[6] chromium (III)-organic acid complexes have also been discovered to be effective catalysts under certain circumstances.[7-9] Chromium (III)-organic acid complexes have been also used extensively in various industrial processes such as tanning, dyeing, hardening photographic emulsion, etc.

EXPERIMENTAL

Reduction of CrO_3 by Ethanol in the Presence of Benzoic Acid

The chromium complexes were characterized by DSC (Differential Scanning Calorimetry), Mass spectroscopy, FAB (Fast Atomic Bombardment) Proton Nuclear Magnetic Resonance (^{1}HNMR) spectrometry, FTIR (Fourier Transform Infrared Spectrophotometer), ICP-OES "Inductively coupled plasma optical emission spectroscopy", and Elemental analysis (C&H). The lability and Kinetics energy properties of complexes formed are examined in the research.

Table-1: Details of Samples and their Identification

S. No.	ID of Samples	CrO$_3$: Benzoic Acid: Solvent (Molar ratio)	Taken Amount (g) of CrO$_3$: Benzoic acid	Yield	Color
1.	BA1	CrO$_3$: Hben: H$_2$O (1:1)	1:1.22	1.20g, 54%	Yellow
2.	BA2	CrO$_3$: Hben: H$_2$O (1:2)	1:2.44	2.00g, 58%	Yellowish-green
3.	BA3	CrO$_3$: Hben: H$_2$O (1:3)	1:3.66	3.49g, 75%	Yellowish-green

Characterization of Samples by Elemental Analysis (C&H) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Sophisticated Analytical Instrument Facility (SAIF) at the Central Drug Research Institute in Lucknow, India, performed the elemental analysis (C&H). Sophisticated Analytical Instrument Facility (SAIF) at the Indian Institute of Technology, Madras, India, used Perkin Elmer 5300 DV (Dual vision) ICP-OES instruments to record samples diluted in acids and containing plasma of argon.

RESULTS AND DISCUSSION

Elemental (C and H %) and ICP-OES (Cr %) Analysis of Complexes

Analysis of metal complexes is reported in Table-2 using ICP-OES and C&H data. The compounds produced have been strongly colored and insoluble in water and ordinary organic solvents, however DMSO at room temperature may dissolve these complexes. It was discovered that the amount of coordinating ben-ligands in the complexes rose proportionately as Cr: acid molar ratio raised. In the Cr/benzoic acid-water (Cr/Hben-water) system, the chromium concentration also rose correspondingly, indicating that there was an increase in the metal complexes' degree of polymerization.

Table-2: Elemental(C & H) and ICP-OES Analytical Data of Metal Complexes

S. No.	Id's of Sample	Found (Calculated) (%)			Molecular Formula
		Cr	H	C	
1.	BA1	16.10(16.61)	4.62(4.79)	39.86(40.26)	C$_{42}$ H$_{60}$ Cr$_4$ O$_{30}$
2.	BA2	18.02(18.99)	4.05(4.16)	43.81(42.95)	C$_{49}$ H$_{57}$ Cr$_5$ O$_{29}$
3.	BA3	19.05(19.57)	3.90(4.14)	40.84(42.16)	C$_{56}$H$_{66}$ Cr$_6$ O$_{34}$

Characterization of Samples by UV-VIS Spectrophotometry

UV-VIS Spectra recorded on ECIL, Hyderabad, Double beam Spectrophotometer UV5704SS, in the range 200-650nm in the Department of Chemistry, IIT(ISM) Dhanbad, India.

UV-VIS Analysis/ Interpretation of Metal Complexes

This has been stated[11] that for the solution, which was generated by dissolving active Cr(III)-hydroxide in an ethanolic solution of Hben the electronic spectra show absorption maxima at 436 along with 587 nm. The two maxima are located in the vicinity of the d-d transitions of octahedral chromium complexes, namely the $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ d-d transitions. It has also been hypothesized that such solutions include a combination of low oligomeric Cr(III) complexes, which exist as anionic and ion partners. There are two bands in the UV visible spectrum of all complexes that may be recognized as the $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ d-d transitions of the octahedral complexes. At 587 and 429 nm, in aqueous solution chromium shows bands that are indicative of oligomeric species, most likely hexamer, tetramer, or trimer complexes in Cr/benzoic acid solutions (Cr/Hben).

Table 3: UV-VIS Spectral Data of Chromium Complexes in DMSO

S. No.	Sample ID	λ_{max} nm (logε)
1.	BA1	552.5(0.551),495(0.548), 526.5(0.543), 520.0(0.496), 516.5(0.470), 586.5(0.440),461.0(0.440),443.5(0.409),344.5(0.398), 338.5(0.388)
2.	BA2	442.5(0.747), 429.5(0.744), 425.0(0.739), 416.5(0.735), 454.5(0.716), 404.5(0.715),497.5(0.555), 306.5(0.487), 344.5(0.485), 299.0(0.482)
3.	BA3	552.5(0.465), 495(0.463), 526.5(0.434), 520.0(0.434), 516.5(0.428), 586.5(0.412),461.0(0.391), 443.5(0.387), 344.5(0.377), 338.5(0.374)

Characterization of Complexes by Fourier Transform Infrared Spectrophotometry (FTIR)
We used the Perkin Elmer spectrum-2000, FTIR (Fourier Transform Infrared) spectrometer with an auto mode to record the infrared spectra of solid materials from the 4000-400cm^{-1} range on the KBr pellets.

FTIR Studies of Cr/ Hben Complexes
Table-3 represents the FTIR spectra of benzoic acid and its Cr/Hben complexes.

Table-4: FTIR Spectral Data of Cr/ Hben Complexes and their Assignment in cm^{-1}

S. No.	ID's of Sample	ν (Cr-O)	ν (-COO)	ν (C-O)	ν (C=O)	δ(O-C=O) +ν (Cr-O)
1.	Benzoic Acid	-------	1424,1584	1312	1695	------
2.	BA1	684,668,553	1423,1584	1293	1690	810
3.	BA2	684,668,553	1423,1584	1293	1690	810
4.	BA3	684,668,553	1422,1584	1293	1688	810

C=O as well as C-O stretching frequencies of benzoic acid's carboxyl group are ascribed the distinctive absorption peaks at 1312 and 1695 cm^{-1}. In benzoic acid, the carboxyl group's ν (-COO) stretching frequency is responsible for the absorption peak at 1584 and1424 cm^{-1}, There is a large band of absorption about 2555 and 3072 cm^{-1} due to the carboxyl group's O-H stretching. An unsaturated aromatic ring is confirmed by the absence of bands between 1680 and 1630 cm^{-1}. The aromatic ring's ν(C=C) and ν (C-H) vibrational frequencies are given to 1602 and 3072 cm^{-1}, respectively. At 1584 and 1526 cm^{-1}, a shoulder is noticed as a stretching vibration of the bridging COO- group, and at 1424 and 1415 cm^{-1}, a strong peak is observed, with 1650 cm^{-1}strong peak because of ν (O-H) of water. C=O stretching is responsible for the band at 1690 and 1592 cm^{-1}.[12] The C-O carboxyl group is responsible for the absorption bands ranging from 1280 to 1293 cm^{-1}, representing the possibility of –COO coordination with the metal ion. Shifts in the frequency of the metal ions suggest that they are involved in complex formation. Phenyl ring vibrations are detected in the 1026-1101 cm^{-1} and 720 cm^{-1} regions of the complexes. Aromatic ν (C-H) is represented by bands of medium intensity in the 3012-3072 cm^{-1} region. This product has been generated, according to the spectra of metal complexes, which show the presence of new bands in the 527-689 cm^{-1} range due to (Cr-O).[13]

Characterization of Complexes by Proton Nuclear Magnetic Resonance (^{1}HNMR) Spectrometry
Tetra Methyl Silane (TMS) was used as an internal standard at the Sophisticated Analytical Instrument Facility (SAIF), Central Drug Research Institute, in Lucknow, India, for obtaining ^{1}HNMR spectra of complexes in DMSO.

^{1}HNMR Studies of Cr/ Hben Complexes
Proton peaks from distinct groups in the complexes could not be differentiated from one another, according to the experimental data. NMR spectra of complexes were marginally different from those of their ligands. Coordination causes a downfield shift in the spectrum of the aromatic ring's protons, which display a peak around 6.86-8.02 ppm when compared to the free ligand's spectrum.

Characterization of Sample by Fast Atomic Bombardment (FAB) Mass Spectroscopy
"Sophisticated Analytical Instrument Facility (SAIF), Central Drug Research Institute (CDRI), and Lucknow, India, recorded the FAB spectra using Jeol SX-102 (FAB) mass spectrometers.

FAB Mass of Cr/ Hben Complexes
BA1: [Cr$_4$ (C$_7$H$_5$O$_2$)$_6$ (OH)$_6$(H$_2$O)$_6$] .6H$_2$O
Anal: found C, 39.86; Cr, 16.10 H, 4.62;
Calculated for C$_{42}$H$_{60}$Cr$_4$ O$_{30}$: C, 40.26; Cr, 16.61; H, 4.79;
1252 is the total complex's calculated molecular weight; 1250 is the observed Molecular Ion Peak (m/z): Loss of 2H$^+$ fragments might explain the molecular weight discrepancy. Results from the FAB mass analysis were inferred on the basis followed by Barnwal *et al.*[14] on oxo-bridge multinuclear chromium assemblies, like trinuclear complex (m/z; 1329) [Cr$_3$O(acac)$_3$ (OOCC$_{15}$H$_{31}$)$_3$].

Table-5: HNMR Spectral Data of Cr/Hben Complexes and their assignment in δ

S. No.	Complex	Chemical Shift	Assignment
1.	BA1	8.02,7.96,7.93,7.78,7.76,7.74,7.63,7.61,7.59,7.52, 7.49, 7.47, 7.25, 7.22, 3.47, 3.17, 2.72, 2.56, 2.50	7.22-8.02 (4H,ArH), 3.17-3.47 (-OH), 2.50-2.72 (Protio-solvent component)
2.	BA2	7.95,7.60,7.49,2.50	7.49-7.95 (4H,ArH), 7.95 (4H,ArH), 2.50 (-OH)

Table-6: FAB Mass Data of Complex B1

Peak position	Predictable fragmentation types	Computed mass
1250	$Cr_4 (C_7H_5O_2)_6 (OH)_6(H_2O)_6 .6H_2O$	1252
1054	$Cr_4 (C_7H_5O_2)_6 (OH)_6(H_2O)$	1054
898	$Cr_4 (C_7H_5O_2)_5 (OH)_5$	898
777	$Cr_4 (C_7H_5O_2)_4 (OH)_5$	777
672	$Cr_3 (C_7H_5O_2)_4 (OH)_2$	674
551	$Cr_3 (C_7H_5O_2)_3 (OH)_2$	553
431	$Cr_3 (C_7H_5O_2)_2 (OH)_2$	432
307	$Cr (C_7H_5O_2)_2 (OH)$	311
289	$Cr (C_7H_5O_2)_2$	294

BA2: $[Cr_5 (C_7H_5O_2)_7 (OH)_8 (H_2O)_7]$
Anal: found C, 43.81; Cr, 18.02 H, 4.05.
Calculated for $C_{49}H_{57}Cr_5 O_{29}$: C, 42.95; Cr, 18.99; H, 4.16;
1369 is the total complex's calculated molecular weight; 1360 is the experiential Molecular Ion Peak (m/z):
A half-molecular water loss may be associated with the molecular weight differential.

Table-7: FAB Mass Data of Complex BA2

Peak Position	Predictable Fragmentation Types	Estimated Mass
1360	$Cr_5 (C_7H_5O_2)_7 (OH)_8 (H_2O)_7$	1369
1238	$Cr_5 (C_7H_5O_2)_7 (OH)_8$	1243
1188	$Cr_4 (C_7H_5O_2)_7 (OH)_8$	1191
1068	$Cr_4 (C_7H_5O_2)_6 (OH)_8$	1070
1014	$Cr_4 (C_7H_5O_2)_6 (OH)_5$	1019
898	$Cr_4 (C_7H_5O_2)_5 (OH)_5$	898
778	$Cr_4 (C_7H_5O_2)_4 (OH)_5$	777
645	$Cr_4 (C_7H_5O_2)_3 (OH)_5$	656
535	$Cr_4 (C_7H_5O_2)_2 (OH)_5$	535
416	$Cr_4 (C_7H_5O_2) (OH)_5$	414
325	$Cr_3 (C_7H_5O_2) (OH)_3$	328
154	$Cr_2 (OH)_3$	155

BA3: $[Cr_6 (C_7H_5O_2)_8 (OH)_{10} (H_2O)_8]$
Anal.: found C, 40.84; Cr, 19.05 H, 3.90;
Calculated for $C_{56}H_{66}Cr_6 O_{34}$: C, 42.16; Cr, 19.57; H, 4.14;
Complex calculated molecular weight = 1594

Characterization of the Sample by Differential Scanning Calorimetry (DSC)
On Perkin Elmer's DSC-7, chromium complexes 'DSC has been performed at the Indian School of Mines University, Dhanbad. The following procedures have been unutilized in every case:
Aluminum (perforated) = Sample pan;
50°C/Min=Scan rate; 50°C=Start temperature; 450°C=End temperature.

Cr/Hben Complexes
From the DSC thermograms, kinetic parameters- lnK_0, Ea (activation energy), ΔH(enthalpy), and order of reaction (n) of decomposition could be calculated. In all cases of Cr/Hben-water complexes the first and second step decomposition, associated with the endothermic process, showed a high value of activation

energy. It may due to polymeric (BA1-tetramer), (BA2-pentamer), (and BA3-hexamer) in nature. In all cases Cr/Hben-TAA complexes second step decomposition associated with the exothermic process and heat flow take place at 363.57, 345.55, and 313.1ºC respectively. An endothermic reaction with low activation energy indicates the complexes' sturdiness in the first stage. Following the first and second order of reaction, decomposition occurs. In most cases, the first stage of the breakdown process is connected with an endothermic activity, while the second step is often related to an exothermic process. As the scanning only went up to 450 °C, it was unable to capture the last step change of the Cr/Hben complexes, which occur naturally as tetramers, pentamers, and hexamers. Table-8 contains an illustration of the related kinetic parameters.

Table-8: Kinetic Parameters of Cr/Hben Complexes Obtained from DSC Thermogram"

Sample Code	Temperature Range (ºC)	Peak Temp. (ºC)	Change in Enthalpy (ΔH) (J/g)	Activation Energy (Ea) (KJ/mol)	Order of Reaction
BA1A	113.75-126.87	122.57	50.02	1395.3±30.14	0.7±0.01
BA1B	198.88-229.86	217.1	13.51	380.16±30.14	1.4±0.01
BA2A	112.68-138.91	128.63	118.17	833.64±18	1.56±0.03
BA2B	231.33- 259.8	250.55	23.67	382.04±8.25	0.57±0.01
BA3A	114- 135.64	127.19	114.78	888.48±19.19	1.47±0.03
BA3B	235.25-256.25	249.35	25.79	284.07±6.13	0.47±0.01

Lability of the Chromium (III) Complexes from DSC Results
According to reports, a complex is said to be inert if the activation energy (Ea) of both the process that forms it and the reaction that breaks it down is high then, the compound is produced, and it slowly decomposed. The energy required for the production and breakdown of a labile complex is quite low. Because of this, the equilibria of creation and breakdown of the complex are quickly formed (at 300 Kelvin, reactions with Ea. less than 25 KJ/mol are fast).[15] This was also noticed that the covalent coordinate bond with an energy of 20-80 Kcal/mol shows high lability with stability with the first-row metal-ligand bond, with the second row it shows medium lability and high stability, while the third row shows low lability and high stability. These findings were based on observations of the first, second, and third rows of metal-ligand bonds.[16] There are a few additional systems, including porphyrin complexes, that exhibit a labile kinetic behavior that is comparable to that of nicotinic acid and Cr (III) – Schiff's base complexes, which has led to the observation of a quick reaction rate between the two. Most reports indicate that the water molecules in the inner sphere of chromium (III) octahedral complexes cannot be substituted by other ligands, but the Aqua (ethylenediaminetriacetatoacetic acid) chromium complexes with five coordinates of EDTA and one molecule of water, show suddenly rapid substitution rates with numerous anionic ligands. It has been suggested that the strain present in the complexes may be responsible for this rapid reaction rate.[17]

Lability of Cr/Hben Complexes
The activation energy of Cr/Hben complexes was: BA1 (380-1395.3KJ/mol), BA2 (382.04-833.64 KJ/mol), BA3 (284.07-888.48 KJ/mol), A reaction between CrO_3 (in water) and benzoic acid (in ethanol), Cr/Hben-water, gave precipitate when refluxed. Precipitate chemical composition closely matched that of the tetrameric species BA1 with monodentate ben- and OH-ligands when the molar ratio was 1:1. When the molar ratio in the Cr/Hben-water was increased to 1:2 the reaction product, BA2, agreed with the pentameric species featuring monodentate ben$^-$ and OH$^-$ ligands. Whereas, the chemical composition of the precipitate, BA3, obtained from the molar ratio of 1:3 closely agreed with the hexameric OH$^-$ bridged Cr (III) complex. Thus, the complexes of Cr/Hben-water system with mol ratios 1:1, 1:2, and 1:3 are probably polymeric species and their polymeric character may be based on Cr-OH-Cr bridges. The $^4A_{2g} \rightarrow ^4T_{1g}$ and $^4A_{2g} \rightarrow ^4T_{2g}$ d-d transitions of octahedral chromium complexes may be ascribed to two bands in the 470-500 and 525-640nm ranges of the UV-visible spectra of all complexes. In an aqueous solution, Chromium has bands at 587 and 429 nm that are typical of oligomeric species, most likely hexamer, tetramer, or trimer complexes. In the infrared range of the spectrum, Asymmetric and symmetric stretching vibrations of the bridging COO- group were observed in Cr/Hben complexes. The coordination of –COO to the metal ion was shown by absorption bands in the 1280-1293 cm^{-1} range, which was ascribed to the C-O carboxyl

group. It was found that complexes had wide absorptions in the region of 3206-3308 cm^{-1}, which suggested the existence of a coordinated water molecule. Sharp and more defined IR spectra may be due to the polymeric nature of these complexes, based on Cr-OH-Cr bridges. NMR of Cr/Hben, deprotonation of –COOH group was noticed. The peak at 6.86 to 8.02 ppm is due to the aromatic ring proton. When the spectrum of the complex is compared with the spectrum of the free ligand a downfield shift caused by coordination was verified. The complexes'-Mass molecular formula generated might be anticipated based on the findings of this study. Cr/benzoic acid-water (Cr/Hben-water) complexes show very high molecular weights, which may be due to the polymeric nature of complexes.

BA1: $[Cr_4 (C_7H_5O_2)_6 (OH)_6 (H_2O)_6]$.$6H_2O$; BA2: $[Cr_5 (C_7H_5O_2)_7 (OH)_8 (H_2O)_7]$;

BA3: $[Cr_6 (C_7H_5O_2)_8 (OH)_{10} (H_2O)_8]$

From the DSC thermograms of the complexes, kinetic parameters-lnK_0Ea (activation energy), ΔH(enthalpy), and order of reaction (n) of decomposition could be calculated. In all cases of Cr/Hben-water complexes, the first and second step decomposition which were endothermic gave a high value of activation energy. It may due to polymeric BA1)-tetramer, BA2-pentamer, BA3-hexamer) in nature. Lability prediction from DSC of Cr/Hben complexes indicated that all water-based complexes were labile to some extent.

CONCLUSION

Complexes were formed with CrO_3 and benzoic acid in an aqueous medium, the complexes formed were different and with a varying molar ratio of the reactants. Polymeric-like, tetramer, pentameric, and hexameric complexes were formed. The complexes' lability and kinetics energy may be anticipated from DSC. A few of the complexes produced were found to be labile to some degree.

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