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Preparation and Characterization of Cr(III) Hydroxamate Complexes (Part-I)

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Summary: A number of tris hydroxamate complexes of chromium(III) have been prepared. These compounds have been characterized by micro-analytical data, U.V-visible studies, infrared analysis and magnetic moment studies.
cis and trans isomers were differentiated on the basis of their infrared and U.V-visible spectra. The values of 10 Dq were calculated from the U.V.-vis spectra. Magnetic moment studies confirm octahedral geometry of the Cr(III) hydroxamate complexes.

Introduction

Most of the microbial iron transport compounds contain three hydroxamate groups, which coordinate ferric iron tetrahedrally and two important classes of these compounds are the ferrichromes and the ferrioxamines. In fact, many of structure-function relationship of the ferrichromes and the ferrioxamines (sidero chromes) [1] can not be answered because of the kinetic lability of these high spin Iron(III) complexes. Substitution of chromic ion increases the possibility of isolating coordination isomers of these biological iron transport compounds. X-ray crystallographic investigation have shown that ferrichromes A has the -cis configuration [2], while trisbenzohydroxamate iron (III) crystalizes in a racemic cis form [3]. Detailed research has been carried out to investigate fully the coordination geometries of diferrisiderochromes with some kinetically inert trivalent metal ion [4-7].

In this paper we report the preparation and characterization of a number of tris chromium (III) hydroxamate complexes. These complexes have been characterized by spectroscopic and analytical data.

Experimental

All the hydroxamic acids used in this work were synthesized in our laboratory, by the literature method [8], while $Cr(Co)_6$ were purchased commercially.

Physical Method:

Infrared spectra were recorded as KBr and CsI discs on a Perkin- Elmer 283 B Instrument. U.V-visible spetra were recorded on a Perkin-Elmer 552 spectrophotometer. Magnetic moment studies were carried out on a Newport instruments Gouy balance.

Preparation of Complexes:

The hydroxamate ligands aceto hydroxamic acid (AHA), propiono hydroxamic acid (PHA), stearohydroxamic acid (SHA), methyl aceto hydroxamic acid (MAHA), and phenyl benzohydroxamic acid (PBHA) were prepared by the literature method [8]. The chromium (III) complexes of these hydroxamate ligand were prepared by a general method devised in our own laboratory. 0.1 mol $Cr(CO)_6$ in 50 ml of acetonitrile was added to 0.3 mol of the hydroxamate ligand in 100 ml of acetonitrile, stirred under nitrogen in the presence of U.V. irradiation for 36 hours. A blue-green precipitate resulted. The precipitate was filtered and washed thoroughly with pentane. The precipitate was dried and stored in dessicator over calcium chloride.

Results and Discussion

Analytical data and physical properties for the prepared complexes are presented in Table-1. The infrared spectra of these compounds were recorded as KBr discs in the region of 4000 cm^{-1} - 200 cm^{-1}. With the hydroxamate ligands chosen (AHA, PHA and SHA) only two geometrical isomers are possible i.e. cis sand trans. The trans isomer should have effectively no symmetry, assuming planar chelate rings and free rotation of the substituted R- groups (RCONHOH). The effective symmetry of the cis isomer would be C_3 with the

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Table 1: Microanalysis, Color, Melting points, and magnetic moments of the Chromium(III) hydroxamates.

Compound	Analysis(%) calculated and Found			Color	M.P. °C	Magnetic moment (B.M.)
	C	H	N			
$Cr(AHA)_3$	24.82 24.45	4.82 4.61	14.38 14.78	Blue/Green	187-188	3.79
$Cr(PHA)_3.H_2O$	32.33 32.50	5.99 6.45	12.57 12.76	Blue/Green	184-185	3.78
$Cr(SNA)_3$	67.21 67.15	11.41 11.71	4.35 3.51	Green	180-181	3.82
$Cr(MAHA)_3.H_2O$	32.33 32.47	5.98 5.69	12.57 12.76	Blue/Green	189-190	3.78
$Cr(PBHA)_3$	68.03 67.72	4.36 4.67	6.10 5.96	Blue/Green	191-192	3.84

same assumption. Since the trans isomer of the Cr(III) hydroxamates ($Cr(AHA)_3$, $Cr(PHA)_3$ and $Cr(SHA)_3$ possesses an effective symmetry, skeletal modes symmetrical with respect to inversion are infrared inactive and those antisymmetrical are infrared active.

N-H Vibration

A couplingof the three trans N-H vibrations of the Cr(III) hydroxamates yield symmetric and antisymmetric vibrations. Only the latter being infrared active at 3200 cm^{-1}. In the cis Cr(III) hydroxamates both symmetric and antisymetric NH vibration results in a change in dipole moment and so far infrared active. The spectrum of these compounds shows an unresolved shoulder at 3205 cm^{-1} and a broad peak with a maximum at 3162 cm^{-1} in the case of $Cr(AHA)_3$.

Cr-O Vibration:

The two Cr-O streching modes of cis Cr(III) hydroxamate are both infrared active at 438 and 479 cm^{-1}. They are separated by approximately 40 cm^{-1}. Such a large splitting may be ascribed to a large repulsive force between two neighbouring oxygen of the hydroxamate ligands. The trans isomers of the Cr(III) hydroxamate in all cases exhibited only one Cr-O stretching mode.

U.V-visible absorption spectra:

The U.V-visible spectra of the prepared compounds and its qualitative assignment are given in Table-2. The d^3 configuration configuration as in our case give rise to two quarter terms, 4F and 4P, with 4F the ground term and 4P being 158 higher in energy. The effect of an octahedral ligand field on the two terms results in the splits of 4F into $4A_{2g}$, $4T_{2g}$ and $4T_{1g}$ states where as 4P goes into a $4T_{1g}$ state.

The energies of the three spin allowed d-d bands of the d^3 systems in a field of octahedral symmetry have been determined by using the following equations.

$$\nu_2 = 1/2\,(158 + 30Dq) - 1/2\,[(15B - 10Dq)^2 + 12B.\,10Dq]^{1/2} \quad (1)$$

$$\nu 1 = 10Dq \quad (2)$$

$$B = (2\nu_1{}^2 + \nu_{22} - 3\nu_1\nu_2)/(15\nu_2 - 72\nu_1) \quad (3)$$

Solving the expression of $\nu 2$ in eq. 1 for B, one may base the fitting of the relation in equation 3 values of 10 Dq, B and B_{35} are readily calculated and are presented in Table-2. In case of the Cr(III) hydroxamates the highest energy band $4T_{1g}$ (F) $4A_{2g}$ is obscured as the hydroxamates are U.V. absorbing ligands. The intensity of this band is less

Table 2: U.V.-visible band and its qualitative assignment for Cr(III) hydroxamates.

Compound	Solvent	TRANSITION			10Dq, hk	B_{35}, cm^{-1}	B_{35},hk
		$2T_{2g}$<----$4A_{2g}$	$4T_{2g}$<----$4A_{2g}$	$4T_{1g}$<----$4A_{2g}$			
$Cr(AHA)_3$	Ethanol	593.8	423.1	325.0	16.84	682	0.74
$Cr(PHA)_3$	Ethanol	592.1	420.0	325.0	16.89	698	0.76
$Cr(SHA)_3$	Ethanol	590.4	417.3	320.0	16.93	712	0.78
$Cr(MAHA)_3$	Ethanol	589.1	432.1	325.0	16.84	713	0.78
$Cr(PBHA)_3$	Ethanol	590.1	428.4	320.0	16.70	860	0.94
$Cr(en)^{3+}{}_3$	Ethanol	671.1	457.7	351.5	14.90	615	0.67

Table 3: U.V.-visible Characterization of Cr(III) Hydroxamates

Assigned Configuration[a]	Absorption Max, nm and Extinction coefficient(E)[b]	
	$4T_{1g}$<—— $4A_{2g}$	$4T_{2g}$<—— $4A_{2g}$
trans -$Cr(AHA)_3$	423.1(110.0),	593.4(80.1)
cis -$Cr(AHA)_3$	425.1(112.1),	595.8(80.7)
trans -$Cr(PHA)_3$	420.0(101.9),	592.1(85.2)
cis -$Cr(PHA)_3$	423.8(103.4),	594.3(82.3)
trans -$Cr(SHA)_3$	417.3(101.4),	590.4(82.1)
cis -$Cr(SHA)_3$	419.5(101.6),	592.3(82.3)
trans -$Cr(MAHA)_3$	432.1(48.1),	589.1(68.9)
cis -$Cr(MAHA)_3$	435.1(63.4),	587.9(72.1)
cis -$Cr(MAHA)_3$	434.8(63.7),	588.6(72.2)
trans -$Cr(PBHA)_3$	428.4(49.8),	590.1(70.3)
cis -$Cr(PBHA)_3$	429.9(66.2),	589.3(71.4)
cis -$Cr(PBHA)_3$	429.8(66.9),	589.5(71.5)
trans-$Cr(BHA)_3$	400(117.1),	600(83.1)
cis -$Cr(BHA)_3$	514(121.4),	596 (82.3)

a. AHA = acetohydroxamic acid
PHA = propionohydroxamic acid
MAHA = N-methyl acetohydroxamic acid
BHA = Benzohydroxamic acid
SHA = N-Steareohydroxanic acid
PBHA = N-phenyl benzohydroxamic acid.

b. Data refer to visible region only, units are litre mol^{-1} cm^{-1}

than the intensity of the either of the other two spin allowed bands in agreement with its formulation as a two electron transition. The variation of B_{35} in Table-2 is comparatively small implying that the t_{2g} shell radial function does not change very much from one hydroxamic acid ligand to another. Since the t_{2g} shell has II symmetry, the implication is that II bonding is not very much important in Cr(III) hydroxamates. The U.V-visible spectra of the -cis and -cis isomers should be identical and distinguishable from the -trans and -trans isomer. The cis isomers are expected to have greater extinction coefficient maxima in their spectra than the trans isomers. As shown in Table-3, the diastereo isomers of $Cr(MAHA)_3$ and $Cr(PBH)_3$ verifies the cis isomers to have greater extinction coefficient than the trans isomers in their electronic absorption spectra.

Magnetic moment studies:

The Magnetic moment of the synthesised compounds were measured. The results are given in Table-4. The magnetic moment properties of the octahedral Cr(III) hydroxamates, like other d^3 systems, are simple as shown in the orbital splitting diagram (Fig. 1), that all such complexes must have three unpaired electron irrespectiveof the ligand field.

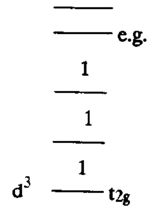

Fig. 1.

It is obvious from Fig. 1, that all the three electrons in the d orbital will naturally enter the more stable t_{2g} orbital with their spin parallel and

Table 4: Theoretical and Experimental moments(BM) of Cr(III).

Ion	Ground State Quantum S	Numbers L	Spectronic Symbols	μs	$\mu S+L$	Observed Moment
Cr^{3+}	3/2	3	^4F	3.87	5.20	3.80

this is true irrespective of the crystal field strength. In octahedral environments of a d^3 ion like Cr(III), the orbital contribution is introduced in opposition to the spin contribution. Hence the observed magnetic moment values for Cr(III) hydroxamate complexes are slightly bellow the theoretical values.

The magnetic moments values are between 3.78-3.84 BM, which closely follows, the value calculated according to spin only formula (3.8 BM); consequently, no orbital contribution is expected.

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