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Synthesis and characterization of ternary complexes of chromium(III) with L-histidine and various diols

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Abstract Ternary complexes of Cr(III) with L-histidine monohydrochloride and various diols of the type MAB, MA₂B and MAB₂ were synthesized and characterized in the present study. The structural properties of complexes were derived from the elemental analysis and magnetic characterization. The elemental analysis and magnetic characterization indicated that they have the octahedral stereochemistry with three unpaired electrons. The values of Dq/B were of greater magnitude for MA₂B type species as compared to MAB and MAB₂ species. Values of nephelauxetic ratio β₅₅ (for spin forbidden band) were found to be more than β₃₅ (for spin allowed transition).

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1. Introduction

Ternary transition metal ion complexes of amino acids are of great importance from the biological point of view (Abdel-Mawgoud and Abdel-Hamid, 1987; Seng et al., 2012; Faheim et al., 2013). A thorough literature survey has revealed that little attention has been paid to ternary metal complexes containing amino acids. Equilibrium studies on the Schiff base complex systems of Co, Ni, Cu and Zn(II)-vanillin(van)(A)-L-valine(val)/L-glutamine(gln)/L-glutamic acid(glu)/L-histidine

(his)(B) have been studied (Nair et al., 2007). Ternary complexes of Co(II), Ni(II), Zn(II), Cd(II), Mg(II) and Ca(II) with adenosine-5'-triphosphate (ATP) as the primary ligand and glycine, alanine, valine, norvaline, leucine, serine, methionine, threonine, aspartic acid, uracil and thymine as secondary ligands have also been studied by other workers (Sastry and Gupta, 1998). Copper(II) complexes of amino acids and peptides with the chelating bis(imidazolyl) residues have been reviewed by other researchers (Sovago et al., 2003). Ahmed et al. (1998) studied the mixed ligand complex of Cu, Ni and Co using dicarboxylic amino acids as primary ligands and 8-hydroxyquinoline as secondary ligand (Ahmed et al., 1998). The interaction of some metal ions with aspartic and glutamic acid has also been investigated using infrared photodissociation spectroscopy (O'Brien et al., 2008). Siu et al. (2008) studied the dissociations of two types of copper(II)-containing complexes of tryptophan, tyrosine and phenylalanine (Siu et al., 2008). Mixed metal Zn(II)-molybdenum(IV) peroxo complexes containing glycylglycine, glycine and acetic acid have also been studied (Sastry and Gupta, 1997). A new series

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ternary complexes of Cu(II), Ni(II), Co(II) and Zn(II) have also been designed and synthesized using a Schiff base derived from 4-aminoantipyrine and o-phenylenediamine (Raman et al., 2008). König has also analyzed and reported the spectral data on the complexes of transition metal ions (König, 1971). Transition metal ion complexes of several compounds have also been investigated for various biological activities (Josyphus and Nair, 2010; Mahmud et al., 2010; Gwaram et al., 2012; Zhou et al., 2013). The stability constants of mixed ligand ternary complexes of Ni(II) with histidine and various diols were also determined in the previous literature (Gesawat et al., 2010). Most of these studies have been performed with divalent ions, paying little attention on transition metal ion complexes with trivalent ions like chromium (Mandlik and Aswar, 2003; Maples et al., 2009). In the present research work, we performed the synthesis, evaluated the results of analytical, spectral and magnetic studies and characterization of ternary complexes of Cr(III) (M) with L-histidine (A) and various diols (B) of the type MAB, MAB₂ and MA₂B. The three spin allowed and one spin forbidden transitions were experimentally observed in these complexes. In this treatment, we have tested and applied the methods which may be used to obtain a numerical fit to the relevant experimental data. An interesting check on the accuracy of the method has been provided by calculating the extra band energy.

2. Experimental

2.1. Chemicals

Analytical reagent (AR) grade of Cr(III) chloride and L-histidine monohydrochloride was purchased from S.M. Chemicals (Mumbai, India). Diols (ethane diol, prop-1,2-diol, 2-butene-1,4-diol, but-1,3-diol, pent-2,4-diol and hex-1,6-diol) were purchased from Fluka, AG (Buch, Switzerland).

2.2. Preparation and isolation of complexes

Semi non-aqueous solutions of Cr(III) chloride, L-histidine and diols in the molar concentration ratios of 1:1:1, 1:2:1 and 1:1:2 for MAB, MA₂B and MAB₂ type species, respectively were mixed together in an inert atmosphere, created by bubbling a current of oxygen free nitrogen. The hydrogen ion concentration of the reaction mixture was maintained at around pH 7 by the addition of standard solution of lithium hydroxide. The dilute solution of lithium hydroxide was used to maintain pH of hydrogen ion concentration as it is recommended to tune pH of electrodeposition solutions (Gesawat et al., 2010). The solution thus obtained after removal of slight turbidity was allowed to concentrate slowly at the ambient temperature in vacuum desiccators. The crystalline product was purified by re-crystallization from methanol (Sastri and Gupta, 1998).

2.3. Physical measurements

Cr(III) was estimated by complexometric titrations, nitrogen was estimated by micro-Kjeldhal's method and magnetic moment by Gouy's method (Figgis and Lewis, 1959; Vogel, 1971). The analytical and magnetic moment data are summarized in Table 1. The electronic spectra were recorded in ethanolic solution by spectrophotometer DMR-21 in the range of 300–1000 nm.

3. Results and discussion

The d³ configuration of Cr(III) gave two quartet state and five doublet state ⁴F, ⁴P, ²P, ²G, ²D, ²H and ²F. In an octahedral field, ⁴F was split up into ⁴A₂, ⁴T₁ and ⁴T₂ states (Fowles et al., 1967; Henning et al., 1967). The only other ligand field states that have been observed in Cr(III) spectra are ⁴T₁(P),

Table 1 Analytical data and magnetic moment of ternary complexes of Cr(III) of the type MAB, MA₂B and MAB₂ [M = chromium, A = histidine, B = diol] at 293.15 ± 0.5 K.

Ligand (B)	Mol. Wt.	% Cr(III)		% Nitrogen		% Carbon		% Hydrogen		Magnetic moment (μ) (B.M.)
		Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found	
Ethane-diol	305.1 ^a	17.0	17.0	13.7	13.7	31.4	31.5	5.5	5.6	3.8
	424.2 ^b	12.2	12.2	19.8	19.7	39.6	39.6	4.7	4.7	3.8
	331.0 ^c	15.7	15.6	12.6	12.6	36.2	36.2	5.7	5.7	3.7
Prop-1,2-diol	319.5 ^a	16.2	16.2	13.1	13.2	33.8	33.9	5.9	6.0	3.9
	438.6 ^b	11.8	11.8	19.1	19.0	41.0	41.0	5.0	5.0	3.8
	359.6 ^c	14.4	14.4	11.6	11.7	40.0	40.0	6.4	6.5	3.7
2-Butene-1,4-diol	331.0 ^a	15.7	15.7	12.6	12.7	36.2	36.2	5.7	5.8	3.8
	451.2 ^b	11.5	11.5	18.6	18.6	42.5	43.7	4.8	4.9	3.8
	384.0 ^c	13.5	13.5	10.8	10.9	43.7	43.8	5.9	6.0	3.7
But-1,3-diol	333.2 ^a	15.6	15.6	12.6	12.6	36.0	36.0	6.3	6.3	3.7
	453.0 ^b	11.4	11.4	18.5	18.5	42.3	42.4	5.3	5.2	3.8
	388.9 ^c	13.3	13.4	10.8	10.7	43.2	43.1	6.9	6.9	3.7
Pent-2,4-diol	347.1 ^a	14.9	15.0	12.1	12.0	38.0	38.0	6.0	6.0	3.7
	467.8 ^b	11.1	11.0	17.9	17.9	43.6	43.5	5.5	5.5	3.8
	417.4 ^c	12.4	12.3	10.0	9.9	46.0	46.1	7.4	7.4	3.8
Hex-1,6-diol	361.0 ^a	14.4	14.4	11.6	11.6	39.8	39.9	6.9	6.9	3.8
	482.1 ^b	10.7	10.7	17.4	17.3	43.6	43.5	5.5	5.5	3.8
	445.2 ^c	11.6	11.7	9.4	9.4	48.5	48.5	7.8	7.9	3.8

^a Ternary complex MAB.

^b Complex MA₂B.

^c Complex MAB₂.

2E_1 , 2T_1 and 2T_2 derived from 2G state. Experimentally, we have observed three spin allowed transition ${}^4A_2 \rightarrow {}^4T_2$ at around $18,000\text{ cm}^{-1}$, ${}^4A_2 \rightarrow {}^4T_1(F)$ at $34,000\text{ cm}^{-1}$, ${}^4A_2 \rightarrow {}^4T_1(P)$ at around $39,000\text{ cm}^{-1}$ and a spin forbidden due to transition ${}^4A_2 \rightarrow {}^2E$ at around $12,800\text{ cm}^{-1}$. These transitions have also been calculated by using numerical fitting method by employing following equations (Figgis and Lewis, 1959; Fowles et al., 1967; Henning et al., 1967; Konig, 1971; Vogel, 1971; Raman et al., 2008):

$$\vartheta_1 = 10 Dq \quad (1)$$

$$\vartheta_2 = \frac{1}{2}(15B + 30Dq) - \frac{1}{2}[(15B - 10Dq)^2 + 12B \times 10Dq]^{1/2} \quad (2)$$

$$\vartheta_3 = \frac{1}{2}(15B + 30Dq) + \frac{1}{2}[(15B - 10Dq)^2 + 12B \times 10Dq]^{1/2} \quad (3)$$

$$B = \frac{\vartheta_2 + \vartheta_3 - 3\vartheta_1}{15} \quad (4)$$

The results are summarized in Table 2.

The nephelauxetic ratio β_{35} was computed by using the relationship:

$$\beta_{35} = \frac{B_{35}}{B_0} \quad (5)$$

(where B_{35} for spin allowed bands, B_0 for free Cr(III) ion at 920 cm^{-1}) and β_{55} , nephelauxetic ratio was obtained by using the transition ${}^4A_2 \rightarrow {}^2E$ (spin forbidden) by employing the relationship (Jorgensen, 1962).

$$\beta_{55} = \frac{B_{55}}{B_0} \quad (6)$$

B_{55} has been calculated from spin forbidden band (${}^4A_2 \rightarrow {}^2E$). The molar extinction coefficient (ϵ) was calculated by nephelauxetic ratio observed by spin allowed and spin forbidden bands using $[\epsilon = (1 - \beta_{35}/\beta_{55})]$ (Sugano and Peter, 1961). The percentage of covalency character was also calculated and summarized in Table 3.

The value of β for complexes was less than that of free ion clearly indicating that as a result of complexation, the metal orbitals expand and this cause the nephelauxetic effect. The magnitude of nephelauxetic effect $(1 - \beta)$ showed the trend in the incidence of covalent character in the metal–ligand bond.

Cr(III) ion (d^3 ion) is a hard metal-ion and thus naturally prefers hard ligand centers for coordination. L-histidine has additional coordination sites in addition to normal amino nitrogen and carboxylate oxygen informed secondary and tertiary nitrogen of imidazole moiety. The pH titration studies have been carried out in detail and their results point out that the secondary nitrogen of imidazole moiety liberates proton even at pH lower than 7. Thus the complexes which have been isolated in the pH range 6.5–7.5 have unidentate carboxylate coordinate and coordination from secondary nitrogen from imidazole moiety. The structure of histidine is such that all the three nitrogen atoms present in the molecule cannot interact simultaneously as these do not lie in a plane. The presence of diols moiety with oxygen donor atoms restricts the further coordination of nitrogen atom, as the coordination affinity of oxygen for Cr(III) is much more than that of nitrogen. The pseudo-aromaticity of imidazole contributes partially for increased covalency of histidine chelates as compared to similar chelates with alanine. The possible structural formulae of these complexes are given in Fig. 1.

Table 2 Experimental and calculated transition energies, values for parameters B_{35} , $10 Dq$ (cm^{-1}) and β_{35} of ternary complexes with Cr(III) of the type MAB, MA_2B and MAB_2 [M = chromium, A = histidine, B = diols].

Ligand (B)	Transition energy						B_{35}	β_{35}
	${}^4A_2 \rightarrow {}^4T_2$		${}^4A_2 \rightarrow {}^4T_1(F)$		${}^4A_2 \rightarrow {}^4T_1(P)$			
	Obs.	Calc. (Dq)	Obs.	Calc.	Obs.	Calc.		
Ethane-diol	18,604 ^a	10	24,096	24,090	39,375	39,380	511	0.555
	19,236 ^b	10	25,354	25,132	40,640	40,861	552	0.600
	18804 ^c	10	25,652	25,702	40,852	40,792	673	0.731
Prop-1,2-diol	18,264 ^a	10	24,691	24,694	39,395	39,392	620	0.573
	20,100 ^b	10	26,143	26,869	40,632	41,905	565	0.614
	18691 ^c	10	25,000	25,023	40,103	40,080	602	0.054
2-Butene-1,4-diol	18,691 ^a	10	25,316	25,319	40,381	40,358	541	0.695
	18,433 ^b	10	23,809	23,865	38,978	38,921	499	0.543
	18604 ^c	10	25,641	25,391	40,560	40,608	693	0.753
But-1,3-diol	17,241 ^a	10	23,391	22,801	37,240	37,890	594	0.646
	18,867 ^b	10	25,157	25,276	40,432	40,312	599	0.651
	18540 ^c	10	25,199	24,323	40,329	40,204	661	0.718
Pent-2,4-diol	17,467 ^a	10	23,952	23,440	37,956	38,467	634	0.689
	17,241 ^b	10	23,529	23,088	37,482	37,923	619	0.673
	17543 ^c	10	23,952	23,428	37,942	38,464	618	0.671
Hex-1,6-diol	18,348 ^a	10	24,844	24,706	39,613	39,742	628	0.682
	18,518 ^b	10	25,316	25,223	40,167	40,259	662	0.719
	18,181 ^c	10	24,390	24,151	38,071	39,310	595	0.646

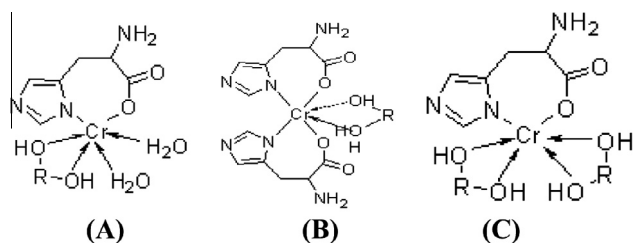
^a Ternary complex MAB.

^b Complex MA_2B .

^c Complex MAB_2 .

Table 3 Transition energy for forbidden band and values of β_{35} , β_{55} , B_{35}^0 and ϵ for ternary complexes of Cr(III) of the type MAB, MA_2B and MAB_2 [M = chromium, A = histidine, B = diols].

Ligand (B)	${}^4A_2 \rightarrow {}^2E$	β_{35}	β_{55}	B_{35}^0	$\epsilon = 1 - \beta_{35}/\beta_{55}$
Ethane-diol	12,970 ^a	0.555	0.735	44.43	0.244
	12,980 ^b	0.601	0.729	39.96	0.176
	12,658 ^c	0.731	0.743	26.87	0.016
Prop-1,2-diol	12,820 ^a	0.674	0.727	32.64	0.073
	12,632 ^b	0.614	0.725	38.54	0.153
	12,158 ^c	0.655	0.720	34.51	0.090
2-Butene-1,4-diol	12,658 ^a	0.696	0.715	30.44	0.027
	12,422 ^b	0.543	0.701	45.74	0.226
	12,820 ^c	0.752	0.704	24.82	0.068
But-1,3-diol	12,820 ^a	0.659	0.732	34.08	0.099
	12,492 ^b	0.651	0.704	34.87	0.075
	12,840 ^c	0.719	0.729	28.21	0.003
Pent-2,4-diol	12,578 ^a	0.691	0.715	30.90	0.034
	12,307 ^b	0.682	0.709	31.76	0.038
	12944 ^c	0.671	0.738	32.87	0.090
Hex-1,6-diol	12,738 ^a	0.682	0.721	31.80	0.055
	12,388 ^b	0.719	0.712	28.06	0.002
	12,500 ^c	0.646	0.707	35.39	0.086

^a Ternary complex MAB.^b Complex MA_2B .^c Complex MAB_2 .**Figure 1** Possible structural formulae of ternary complexes of Cr(III) with L-histidine and various diols at different ratios A (1:1:1), B (1:2:1) and C (1:1:2).

4. Conclusions

Ternary complexes of Cr(III) with L-histidine monohydrochloride and various diols were successfully synthesized and characterized. The values of Dq/B were of greater magnitude for MA_2B type species as compared to MAB and MAB_2 species. Values of nephelauxetic ratio β_{55} (for spin forbidden band) were found more than β_{35} (for spin allowed transition).

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