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Metal Complexes of 8-Amino-7-Hydroxy-4-Methylcoumarin. I. Chromium(III), Iron(III), Cobalt(III), Nickel(II) and Copper(II) Complexes

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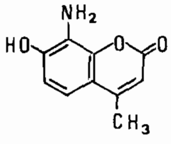
8-Amino-7-hydroxy-4-methylcoumarin has been found to form distinct coloured complexes with Cr^{III}, Fe^{III}, Co^{III}, Ni^{II}, *and* Cu^{II} *metal ions. These complexes have been isolated and characterized by analyses, magnetic, electronic and infrared spectral studies. All the complexes are octahedral except the copper(II) complex which has square planar stereochemistry. The values of splitting energy, ligand field stabilization energy, Racah's parameters and nephelauxetic ratio, have been evaluated in most of the cases. Iron(III) complex is trimeric in nature involving chlorine bridges as evidenced by i.r. studies. Also these studies indicate the coordination of ligand through nitrogen atom. The stability order for metal ions has been drawn on the basis of* $\nu_{assym}(NH_2)$ *vibrations.*

Introduction

The chelating ability of coumarins, derivatives of benzo-α-pyrone, have long been known.[1] Hydroxycoumarins exhibit distinct physiological, photodynamic, bacteriostatic,[2-4] and tubercolostatic[1] activities in vitro to some extent and are potentially useful analytical reagens.[5] They have been successfully used in the detection and determination of many transition metals by gravimetric[6,7] and spectrophotometric[8-10] techniques and many important separations[11] and subsequent estimations have also been performed with their aid. Practically nothing has been described regarding the spectral and magnetic studies of metal complexes of coumarin derivatives.

8-Amino-7-hydroxy-4-methylcoumarin (AHMC) has been used as a chelating reagent for several metal ions.[12-16]



(AHMC)

The present communication deals with the spectral and magnetic properties of AHMC complexes of Cr^{III}, Fe^{III}, Co^{III}, Ni^{II}, and Cu^{II}.

Experimental Section

8-Nitro-7-hydroxy-4-methylcoumarin was prepared by the method of Shah and Mehta,[17] from which the amino compound was obtained by the method of Kumar.[18] All chemicals used were of AnalaR grade. Elemental analyses were performed in Microanalytical Laboratory, Indian Institute of Technology, Kanpur-16, India. Metal estimations were carried out by standard literature methods. Table I records the analytical data of the complexes.

Isolation of the complexes. Monohydroxo bis-(8-amino-7-hydroxy-4-methylcoumarin) monoaquo chromium(III) dihydrate, $[Cr(C_{10}H_8NO_3)_2(OH)(H_2O)]\ 2H_2O$. On mixing 375 ml of 0.02 *M* ethanolic solution of AHMC with 75 ml of an equimolar solution of chromium(III) chloride, a yellow ochre (blackish) coloured solution was obtained between the pH 1.5-3.0. On raising the pH of this solution to ~5.5 by the dropwise addition of sodium hydroxide solution, a greyish coloured precipitate was obtained which changed to green when the pH was again raised to ~7.0 by the addition of sodium hydroxide solution. The precipitate was digested, cooled, filtered off and washed successively with water, ethanol and ether and dried. Loss in weight, on heating the complex between 110-115°C, corresponded to two water molecules. The complex decomposed between 270-300°C.

(*) This work has been taken from the Ph.D. thesis of D.K. Rastogi submitted to the Agra University, Agra (India) in February, 1971.

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Table I. Analytical data of AHMC complexes

Compound		C %	H %	N %	Cl %	H_2O %	Metal %	Yield %
$[Cr(C_{10}H_8NO_3)_2(OH)(H_2O)]2H_2O$	Calcd:	47.71	4.60	5.56	—	7.15	10.33	85
	Found:	47.69	4.48	5.82	—	7.30	10.43	
$[Fe_3(C_{10}H_8NO_3)_5Cl_4]$	Calcd:	47.60	3.17	5.50	11.25	—	13.29	70
	Found:	47.45	3.20	5.67	11.20	—	13.25	
$[Co(C_{10}H_8NO_3)_2(Cl)(H_2O)]$	Calcd:	48.75	3.68	5.68	7.19	—	10.19	80
	Found:	48.63	3.72	5.75	7.29	—	10.20	
$[Ni(C_{10}H_8NO_3)_2(H_2O)_2]$	Calcd:	50.56	4.24	5.89	—	—	12.35	90
	Found:	50.91	4.57	5.90	—	—	12.33	

Bis-(8-amino-7-hydroxy-4-methylcoumarin) iron(III)-μ-dichloro mono-(7-amino-7-hydroxy-4-methylcoumarin) iron(III)-μ-dichloro bis-(8-amino-7-hydroxy-4-methylcoumarin) iron(III), $[Fe_3(C_{10}H_8NO_3)_5Cl_4]$. A brownish-violet colour was observed when 300 ml of a 0.02 *M* ethanolic solution of AHMC were mixed with 75 ml of an equimolar solution of iron(III) chloride and the pH was brought downto ~1.3 by adding dilute hydrochloric acid solution. The reaction mixture was heated on a water bath and the concentrate so obtained was kept in a refrigerator. The deep brownish-violet coloured crystals which appeared after a couple of days were filtered off, washed thoroughly with water, ethanol and ether and dried. The complex decomposed between 310-340°C.

Monochlorobis-(8-amino-7-hydroxy-4-methylcoumarin) monoaquo cobalt(III), $[Co(C_{10}H_8NO_3)_2(Cl)(H_2O)]$. 75 ml of a 0.02 *M* aqueous solution of cobalt nitrawere added to 300 ml of an equimolar ethanolic solution of AHMC, a pink colour was found to develop when the pH of the reaction mixture was brought down to ~3.0 by adding dilute hydrochloric acid solution. A vigorous stream of air was bubbled through the solution for about 48 hours and then it was concentrated by evaporation on a water bath, which on cooling yielded pink coloured crystals. The crystals so obtained were washed several times with water and ethanol-ether mixture and dried. The complex melted above 350°C.

Bis-(8-amino-7-hydroxy-4-methylcoumarin) diaquo nickel(II), $[Ni(C_{10}H_8NO_3)_2(H_2O)_2]$. A light green coloured precipitate was obtained at pH ~9.2 on adding few drops of ammonia solution to a mixture of 75 ml of 0.02 *M* aqueous solution of nickel sulphate and 300 ml of an equimolar ethanolic solution of AHMC. The precipitate was digested, cooled, filtered off and washed successively with water, ethanol and ether and dried. The complex changed its colour to brown at 205° and decomposed at 245°C.

Bis-(8-amino-7-hydroxy-4-methylcoumarin) copper-(II), $Cu(C_{10}H_8NO_3)_2$. This compound was prepared by the method reported earlier.[19]

Magnetic Susceptibility Measurements. The magnetic measurements at room temperature were made on powder form of the complexes employing Gouy's method. Mercury(II) tetrathiocyanato cobaltate(II) ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. units at 293°K) was used as a calibrant. The data are given in Table II.

Electronic Spectral Measurements. A Cary-14 recording spectrophotometer was used to record the electronic spectra of Cr^{III}, Ni^{II}, and Cu^{II} complexes while the spectra of Fe^{III} and Co^{III} complexes were scanned on Hilger Uvispek spectrophotometer. The bands and relevant ligand field parameters are cited in Table III.

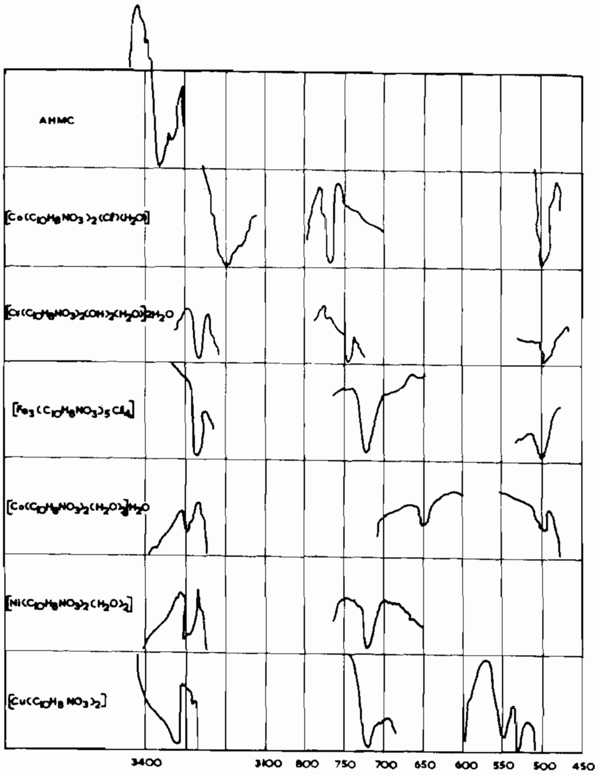

Figure 1. A comparison of $\nu_{assim.}(NH_2)$, $\delta r(NH_2)$ and $\nu(M-N)$ vibrations in the infrared spectra of AHMC complexes.

Infrared Spectral Measurements. The infrared spectra of all the complexes were recorded on a Perkin-Elmer Infracord spectrophotometer, model 521, in KBr pellets and the tentative assignments of the bands are given in Table IV. The comparison of $\nu_{assym}(NH_2)$, $\delta r(NH_2)$ and $\nu(M-N)$ vibrations has been given in Figure 1.

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Table II. Magnetic Susceptibility Data.

Complex	Temp (°K)	$\chi_M \times 10^6$ (c.g.s.) uncorrected	$\chi_M \times 10^6$ (c.g.s.) corrected	μeff (B.M.)	Average μeff (B.M.)
Cr^{III}—AHMC	301	5127	5330	3.60	3.59
	302	5107	5310	3.58	
Fe^{III}—AHMC	302	3432	3592	3.08	3.08
Ni^{II}—AHMC	301.5	3869	4046	3.14	3.13
	302.5	3839	4016	3.12	
Cu^{II}—AHMC	302.5	1504	1645	2.00	1.99
	303.5	1462	1603	1.98	

Table III. Electronic Spectral Data and Relevant Ligand Field Parameters.

Complex	Medium	observed bands (cm^{-1})	Assignment	10Dq (cm^{-1})	L.F.S.E. Kcal/mole	Racah's parameter (cm^{-1})	Nephel-auxetic Ratio (β)
Cr^{III}—AHMC	Nujol-mull	13510	$^4A_{2g} \rightarrow {}^2E_g$	17450	59.8	B= 712	0.69
		17450	$\rightarrow {}^4T_{2g}(F)$				
		27770	$\rightarrow {}^4T_{1g}(F)$				
		37030	$\rightarrow {}^4T_{1g}(P)$				
Fe^{III}—AHMC	Nujol-mull	14000	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$	14000	—	B=1275	0.98
		19200	$\rightarrow {}^4T_{2g}(G)$				
		24300	$\rightarrow {}^4A_{1g}(G)$				
		30300	$\rightarrow {}^4T_{1g}(P)$				
		40000	Charge-transfer				
		47620					
Co^{III}—AHMC	Nujol-mull	11900	$^1A_{1g} \rightarrow {}^3T_{1g}$	25970	29.6	B= 530 C=4690	—
		21280	$\rightarrow {}^1T_{1g}$				
		20770	$\rightarrow {}^1T_{2g}$				
		37040	Charge-transfer				
Ni^{II}—AHMC	Acetone	13830	$^3A_{2g}(F) \rightarrow {}^1E_g(D)$	9402	32.2	B= 960	0.88
		16940	$\rightarrow {}^3T_{1g}(F)$				
		28000	$\rightarrow {}^3T_{1g}(P)$				
Cu^{II}—AHMC	Ethanol	14800	$^2B_{1g} \rightarrow {}^2A_{1g}$	—	—	—	—
		17800	$\rightarrow {}^2E_g$				
		25470	Charge-transfer				
		37030					

Results

Analyses reveal the metal to ligand ratio to be 1:2 in all the complexes but for iron(III) complex in which this ratio corresponds to 3:5.

Chromium(III) ion is expected to show a paramagnetism corresponding to three unpaired electrons in the octahedral environment but in many cases the magnetic moments below spin-only value have been observed[20,21] which may be attributed to the positive spin-orbit coupling constant for the ions having configurations less than d^5 and also to smaller magnetic anisotropy in case of chromium(III), irrespective of the nature of the bond involved. The magnetic moment value for the present complex is 3.59 B.M. The band at 13510 cm^{-1} observed in the electronic spectra of chromium(III) complex is spinforbidden due to $^4A_{2g}(F) \rightarrow {}^2E_g$ transition and the remaining three bands are spin-allowed and may involve the transitions, $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ (17450 cm^{-1}); $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ (27770 cm^{-1}, and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ (37030 cm^{-1}). Using the energies suggested by Figgis,[23] the value of 10 Dq may be derived directly from the first spin-allowed band and the corresponding value of L.F.S.E. has been evaluated as 59.8 Kcal per mole. The value of Racah's interelectronic repulsion parameter (B) is reduced to ca. 69% of the free ion value for Cr^{III} (1030 cm^{-1}).[24] The ratio $^4T_{1g}(F)/{}^4T_{1g}(P)$ is 2.1 suggesting that the latter term would lie at about 37000 cm^{-1}. This value is in close agreement with the observed band at 37030 cm^{-1}.

Iron(III) forms a variety of polynuclear complexes[25-27] which show subnormal magnetic moment ranging from 3.25-3.90 B.M. There is no direct evidence for the actual structure of these complexes but the molecularity which is mostly taken as three is based on the empirical formula only. The complex under study has a magnetic moment value 3.08 B.M. which may possibly be evplained by assuming a trinuclear formula, where the three iron atoms are bound through chlorine bridges (see i.r. discussion). Iron(III) has the ground state ^6S and thus all the absorption bands must, therefore, be spin forbidden. In fact, a very many bands havebeen observed in the electronic spectra of the present complex. The bands beyond 30,000 cm^{-1} may presumably be due to charge transfer. A complete analysis of the ligand field spectrum of this ion has not been possible but an estimate of 10 Dq

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Table IV. Tentative Assignments of Bands in the Infrared Spectra of AHMC and its Complexes (cm^{-1}).

AHMC	Cr^{III}—AHMC	Fe^{III}—AHMC	Co^{III}—AHMC	Ni^{II}—AHMC	Cu^{II}—AHMC	Assignments
3442(s)	3456(s)[a]	—	—	—	—	ν(OH) of phenol
—	3415(s)	—	3411(s)	3415(s)	—	ν(OH) of H_2O
3368(s)	3270(s)	3280(s)	3200(s)[b]	3308(s)	3320(s)	$\nu_{assym}(NH_2)$
3302(s)	3210(s)	3239(s)	—	3230(s)	3215(s)	$\nu_{sym}(NH_2)$
3287(s)				3220(s)		
3238(s)						
3154(s)	3140(m)	3175(s)	3119(s)	3140(s)	3156(s)	ν(C—H)
3140(s)		3128(m)				
1677(s)	1700(s)	1756-1695(sb)	1692(s)	1777(w)	1740(s)	ν(C=O) of ketone
				1708(s)		
		1642(s)				
1614(s)	1600(s)	1615(s)	1606(sb)	1609(s)	1600(s)	$\nu(NH_2)$+conjugated—*o*—hydroxy—phenyl+$\delta(H_2O)$
		1594(s)				
1569(s)	1562(msh)	1564(m)	1490(s)	1571(s)	1572(s)	ν(C—C)
1511(s)	1486(m)	1535(msh)	1445(s)	1536(w)	1534(m)	
1464(s)		1470(m)		1496(s)	1488(s)	
1433(w)	1436(m)	1415(m)	1434(m)	1440(m)	1437(m)	$\delta_{assym}(C—CH_3)$
1380(s)	1382(s)	1384(m)	1384(m)	1388(s)	1380(s)	$\delta_{sym}(C—CH_3)$
	1363(w)		1368(ssh)	1369(s)		
			1347(s)			
1334(s)	—	—	—	—	—	δ(OH) of phenol
1294(s)	1300(m)	1310(m)	1304(s)	1294(s)	1304(s)	ν(C—N)
1240(m)	1220(w)	1254(m)		1229(m)	1224(m)	
1199(m)	—	1150(m)	1144(m)	1132(w)	—	
1145(s)		1132(m)				
		1114(w)				
—	1075(w)	1064(m)	1065(s)	1092(s)	1092(s)	$\delta w(NH_2)$
1040(s)	1055(w)	1034(w)	—	1038(m)	—	
1029(msh)	995(w)[c]	988(w)		1006(m)		
986(s)						
—	932(w)	—	938(m)	935(w)	—	$\delta r(H_2O)$ coordinated water
858(w)	806(w)	890(w)	837(m)	832(m)	840(m)	δ(C—H) out of plane
843(s)		877(w)	810(m)	813(m)	806(m)	
800(s)		846(w)				
794(s)						
—	745(w)[d]	730(w)	770(w)[d]	722(w)	726(w)	$\delta r(NH_2)+\delta w(H_2O)$ coordinated
—	668(w)	—	689(m)	654(m)	—	ν(M—O) of coordinated water
594(m)	548(w)	605(wsh)	563(m)	615(m)	620(w)	
560(m)		592(w)	550(m)	595(m)	610(w)	
534(w)		542(w)	530(m)	535(w)	550(w)	
—	500(wb)[e]	500(w)	508(w)	—	500(w)	ν(M—N)
					480(w)	
407(w)		442(w)	475(m)	—	445(m)	ν(M—O)
— 456(w)	—	—	428(w)	—	420(w)	
— 430(w)	—	315(w)[f]	350(w)	—	—	ν(M—Cl)

s, strons; w, weak; sh, shoulder; b, broad; δr, rocking vibration; δw wagging vibration. [a] ν(M—OH) vibration; [b] $\nu_{assym}(NH_2)$-vibrations; [c] bending δ(M—OH); [d] coupled with ν(M—O) of coordinated water; [e] ν(M—N) and ν(M—O) bands are coupled; [f] bridging ν(M—Cl) vibration band.

~ 14,000 cm^{-1} has been obtained.[28] Taikng this value into account and using the ratio of Dq/B to be as 1.1,[28] the value of B has been estimated as 1275 cm^{-1} as against 1300 cm^{-1}[24] in the free gaseous ion. The nephelauxetic ratio would, therefore, be 0.98.

Cobalt(III) complexes are usually diamagnetic in nature in the octahedral environment. The complex described herein is also diamagnetic ($\chi_g = -0.1523 \times 10^{-6}$ c.g.s. units at 300°K). As expected, the electronic spectra of the present complex is made up of two strong bands appearing at 21,280 cm^{-1} ($^1A_{1g} \rightarrow {}^1T_{1g}$) and 30,770 cm^{-1} ($^1A_{1g} \rightarrow {}^1T_{2g}$). In addition to these, two more bands at 11,900 cm^{-1} and 37,040 cm^{-1} have been observed. The former is a spin-forbidden band involving $^1A_{1g} \rightarrow {}^3T_{1g}$ transition and the latter may be a charge transfer band. The equations suggested by Dingle and Ballhausen[29] for d^6 configuration have been utilised to evaluate the values of 10 Dq, B and C which come out to be 25,970 cm^{-1}, 530 cm^{-1}, 4690 cm^{-1}, respectively. The corresponding value of L.F. S.E. is 29.6 Kcal/mole.

Extensive magnetic studies have been carried out on the octahedral nickel(II) complexes and there is essentially no gap found between the magnetic moment values of 2.8-3.5 B.M. Nyholm[30] has discussed this increase in magnetic moment value from that of the spin-only value because of some «mixing in» of upper states via spin-orbit coupling. The present Ni^{II} complex reveals a magnetic moment of 3.13 B.M. which falls well within this range. The two of the three main bands, now well established for the majority of octahedral Ni^{II} complexes, have been ob-

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served to occur at 16,940 cm^{-1} (ν_3) and 28,000 cm^{-1} (ν_4) in the spectra of the present complex and have been assigned as $^3A_{2g}\rightarrow{}^3T_{1g}(F)$, $^3A_{2g}\rightarrow{}^3T_{1g}(P)$, respectively. In addition to these, the band at 13,830 cm^{-1} (ν_2) may be assigned to spin-forbidden, $^3A_{2g}\rightarrow{}^1E_g(D)$, transition. According to the equations given by Figgis[31] the near infrared band (not observed in the present case) has been theoretically calculated to occur at 8470 cm^{-1} which directly yields the value of 10 Dq. This procedure is not very accurate as it assumes that the lowest energy transition is not perturbed by higher transitions. In practice this perturbation is present to a small extent and can be estimated using Ballhausen's equations.[32] The corrected value of 10 Dq thus comes out to be 9402 cm^{-1}. Making use of this value of 10 Dq, the energies of ν_3 and ν_4 bands have been calculated and checked against the observed values, since this is the justification of having cubic symmetry. The calculated values of ν_3 and ν_4 are 16,920 cm^{-1} and 28,280 cm^{-1}, spectively revealing a close agreement with the experimental values of ν_3 (16,940 cm^{-1}) and ν_4 (28,000 cm^{-1}). The value of B comes out to be 960 cm^{-1} as against 1080 cm^{-1} in free gaseous ion.[24] The ratio of the two values (B) is therefore 0.88. The value of L.F. S.E. has been estimated to be 32.2 Kcal/mole.

No significant conclusion concerning the stereochemistry of Cu^{II} ion can yet be drawn from the magnetic data. The present copper(II) complex has a magnetic moment value 1.99 B.M. Four bands have been observed in the electronic spectra of the present complex at 14,800 cm^{-1}, 17,800 cm^{-1}, 25,470 cm^{-1}, and 37,030 cm^{-1} which correspond to the square planar stereochemistry.[33] The first two may presumably the transitions $^2B_{1g}\rightarrow{}^2A_{1g}$ (14,800 cm^{-1}) $^2B_{1g}\rightarrow{}^2E_g$ (17,800 cm^{-1}) and the other two may be charge-transfer bands. An interesting feature is that the ratio σ_{Cu}/σ_{Ni} between the wave number σ_{Cu} of the principal band of the Cu^{II} complex and σ_{Ni}, the wave number of the first spin-allowed of high-spin octahedral Ni^{II} complex with the same ligand (when the value of 10 Dq is corrected for intermediate coupling effect) would be 1.6-1.8[34] for a highly tetragonal distortion of Cu^{II}. This ratio is in conformity with the present Cu^{II} complex (σ_{Cu}/σ_{Ni} $\sim$1.6) having square-planar stereochemistry which is the extreme case for tetragonal distortion.

Infrared Studies. The infrared spectral studies show that the stretching and deformation OH vibrations of phenol observed in AHMC at 3442 cm^{-1} and 1334 cm^{-1} respectively are absent in the spectra of all the complexes. The disappearance of these bands on complexation is due to the loss of proton suggesting the formation of a metal-oxygen bond in the complexes. The M–O stretching vibration appears as a weak absorption bandat 442 cm^{-1} (Fe^{3+}), 475 cm^{-1} (Co^{3+}), and 445 cm^{-1} (Cu^{2+}). However, in case of Cr^{III} complex this vibration seems to have been coupled with the M–N stretching vibration and appears as a weak broad band at 500 cm^{-1}.

The antisymmetric NH$_2$ stretching vibration appears as a strong absorption band at 3368 cm^{-1} whereas three strong bands at 3302 cm^{-1}, 3287 cm^{-1}, and 3238 cm^{-1} have been observed in the symmetric NH$_2$ vibration region in AHMC. Both the antisymmetric and symmetric NH$_2$ stretching modes in the complexes have been considerably lowered (see Table IV) compared with those in the free ligand and the changes in ν(NH$_2$), δw(NH$_2$), and δr(NH$_2$) vibrations have also been observed. The major cause of this lowering is the drainage of electrons from the nitrogen atom which in turn weakens the N–H bond. It has been suggested that the decrease in N–H stretching frequency is attributed to the increase in the metal-nitrogen bond strength.[35-37] In the present studies ν_{assym}(NH$_2$) frequency is found to decrease in the following order:

$$\mathrm{Co^{III}} > \mathrm{Cr^{III}} > \mathrm{Fe^{III}} > \mathrm{Ni^{II}} > \mathrm{Cu^{II}}$$

The similar order has been drawn by Kobayashi and Fujita.[38] As expected, this vibration in the Cr^{III} complex has been observed at a higher frequency than that in the corresponding Co^{III} complex, because the coordination effect of Cr^{III} ion is considered weaker than that of Co^{III} ion.[38] This is also in agreement with their values of 10 Dq (see Table III). Band assignment for ν(M–N) vibrations in the metal-amine complexes has been a subject of considerable interest and controversy in the recent years. Powell and Sheppard[39] and Nakamoto *et al.*[40] have assigned the bands near 500 cm^{-1} to ν(M–N) modes. In the present studies ν(M–N) vibration has been observed at 508 cm^{-1} (Co^{3+}), 500 cm^{-1} (Cr^{3+}), 500 cm^{-1} (Fe^{3+}), 500 cm^{-1}, and 480 cm^{-1} (Cu^{2+}).

Several halogen bridged complexes are reported in the literature.[41-44] In almost all cases the metal-halogen bridged stretching vibration has been observed in 250-330 cm^{-1} in the Fe^{III} complex indicates the presence of chlorine bridging. A weak absorption band at 350 cm^{-1} has been observed in the Co^{III} complex which may be due to ν(M–Cl) vibration.

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