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COMPLEXES OF COBALT CONTAINING HYDROXAMIC ACID

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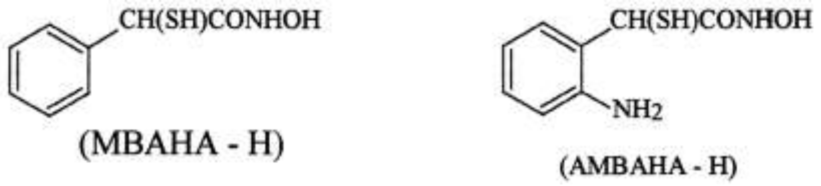
ABSTRACT: The ligands a-mercaptobenzacetohydroxamic acid (MBAHA-H) and 2-amino-α-mercapto-benzacetohydroxamic acid (AMBAHA-H) and their different mixed ligand novel complexes with Co (III) having specific formulae have been synthesized and characterised by elemental analyses, magnetic and conductance measurements, IR and electronic spectral studies. The ligands were found to behave as monobasic tridentate (SO'O donor) and tetradentate (SO' ON donor) manner respectively. All the synthesized Co (III) complexes were non-electrolyte with magnetic moment ranging from 4.6 to 5.4 BM. The structural assessment of the complexes has been carried out based on spectral studies (electronic and infrared) and molar conductivity values. All the complexes were found to be of octahedral geometry.

Key words: Hydroxamic acids, Polydentate ligands, Octahedral complexes, Magnetic moment.

Introduction

The structural modification of organic molecules has considerable biological relevance and their coordination with different metal ions significantly alters the effectiveness of the biomolecules. There is a correlation between the biological activities with geometry of the complexes. Hydroxamic acids are versatile reagents for organic and inorganic analyses[1,2]. Their derivatives are biochemically highly active and find applications in medicinal use[3]. The mercapto group containing derivatives of hydroxamic acid have aroused considerable interests over decades[4]. Hydroxamic acids having one or more –CONHOH groups have been extensively studied as a consequence of their biological, pharmacological, toxicological and pathologicalimportances which are related with their ability to form metal ion complexes[5-7]. Besides, they have a great number of applications in analytical chemistry. Monohydroxamic acids (such as benzohydroxamic acid, $C_6H_5CONHOH$ = BHA) after deprotonation acts as bidentate ligands forming octahedral complexes with a series of metal ions via co-ordination through the two oxygen atoms of the -CONHO- group. This type of coordination with bivalent Ni, Co and Zn ions indicated the formation of octahedral complexes both in the solid state and in solution[8].

In continuation of our work on the complexes with the hydroxamic acid derivative ligands has been characterized in previous studies[9-12], we report here the Co (III) mixed ligand complexes formed by polydentate hydroxamic acids {α-mercaptobenzacetohydroxamic acid (MBAHA-H) and 2-amino-a-mercapto-benzacetohydroxamic acid (AMBAHA-H)} (Fig. 1) taken as the primary ligands (A) and a secondary ligands (B) represented either by chloride, pyridine (py-) or pyridine-N-oxide (py-O-) in this research article. The primary ligand (MBAHA-H) potentially acts as tridentate (SO'O) and (AMBAHA-H) as tetradentate (SO'ON) ligand but all these secondary ligands act as monodentate ligands.



(MBAHA - H) (AMBAHA - H)

Fig. 1

EXPERIMENTAL

Materials

All the chemicals and reagents used were of Analar grade. Anhydrous grade alcohols, DMF, and DMSO were obtained from Fischer scientific. 2-aminobenzhydroxamic acid was obtained from Aldrich (USA). The metal chlorides/acetates used were of BDH AR grade in the present investigation. All reactions and experimental manipulations were carried out at appropriate temperature.

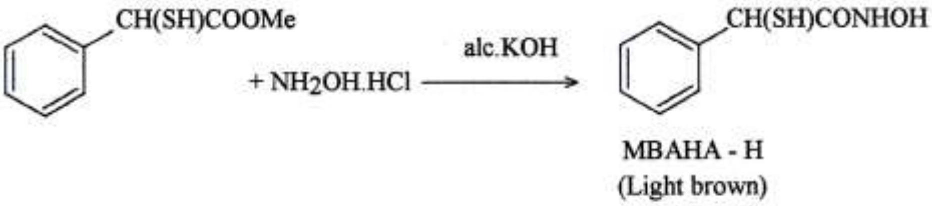
Physico-chemical measurements

Elemental analysis (C, H, S and N) of ligands and complexes was carried out in micro analytical laboratory on Carl-Ebra 1106 elemental analyzer. Metal in the complexes was estimated following standard procedure[13]. The molar conductance measurements were carried out for the 10^{-3} M solutions of complexes in DMSO solvent at 300 K using a Systronics direct reading digital Conductivity Bridge-304 with a dip type cell. The magnetic measurements of the complexes at 300 K were made by Gouy magnetic balance using $Hg[Co(NCS)_4]$ as calibrant. The measured susceptibilities were corrected for diamagnetic susceptibility of the ligand. The IR spectra of ligand and the complexes as nujal-mull smears were recorded in the region 4000-200 cm^{-1} on a Perkin-Elmer 577 spectrophotometer. The electronic spectra of the complexes were recorded on Systronics UV-Visible spectro-photometer Type –119 PC based (λ. = 200-1000 nm & band width 2 nm) using ethanol as the solvent.

Synthesis of Ligand [MBAHA-H = L-H]

The ligand MPA-H was prepared the method reported by Inoue and Yukawa[14]. One mole of KOH (56.10 g) dissolved in 140 mL of methanol was added to a solution of 0.67 moles of hydroxylamine hydrochloride (46.7 g) in methanol. Both solutions were mixed together keeping the temperature range at 35-40°C. The mixture was left in ice-bath for five minutes ensuring the complete precipitation of KC1. Then 0.35 moles of a-mercaptophenyl acetate was added in portions constant shaking and after the addition is complete the solution was filtered immediately through suction. The residue in funnel was washed with little methanol. The filtrate was kept in Erlenmeyer flask for 48 hours. Crystals of potassium salt of the acid were filtered, washed with a little absolute alcohol and dried in air.

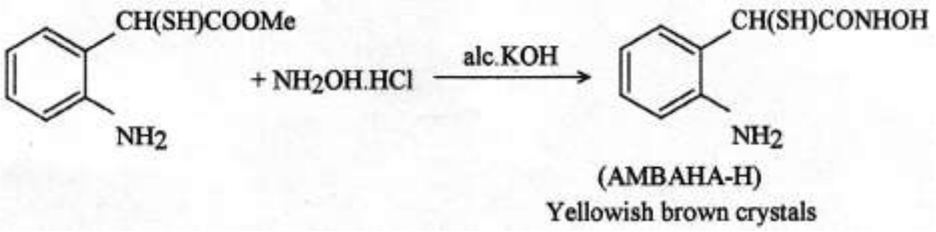
About half of the yield was mixed with 80 mL 1.25 N acetic acid and stirred, while heating until a clear solution was obtained. The solution was allowed to cool at room temperature and finally chilled in ice-bath. The ligand, MBAHA-H, was separated out as light brown crystals. The melting point (decomposition point) was recorded and found to be $186\text{-}188^0$C. The stoichiometry of the synthesis reaction is represented in the form of equation as–



Synthesis of Ligand [AMBAHA-H = L'H]

This was also prepared by the method described above. The alkaline solution of hydroxylamine was prepared as above mixing the methanolic solutions of KOH and hydroxylamine hydrochloride. The solution of 0.175 mole of 2-amino α-mercaptophenyl acetate in methanol was added to it to get the potassium salt of the acid. The free acid was obtained by treating the potassium salt with acetic acid. Yellowish brown crystals ofthe ligand were obtained. The melting point (decomposition point) was recorded and found to be 198-199°C.

The formation of ligand can be represented by the following chemical equation:

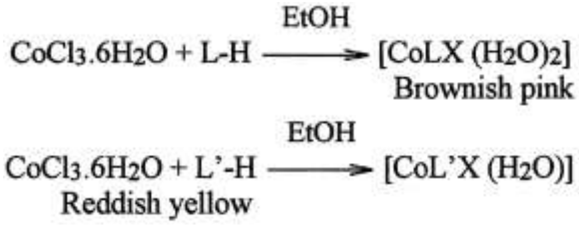


Synthesis of complexes

(A) Synthesis of complexes of type [MLX.H_2O] and

[ML' X] Where, X = Cl

About 0.041 moles of metal chloride were dissolved in 40 mL of distilled water and added to an aqueous ethanolic solution of the ligand (0.40 moles in 35 mL water) slowly with constant shaking. The different coloured heavy precipitate was separated out. It was filtered, washed with distilled water until free from chloride and dried at 140-145°C.



$$CoCl_3.6H_2O + L\text{-}H \xrightarrow{EtOH} [CoLX(H_2O)_2]$$

Brownish pink

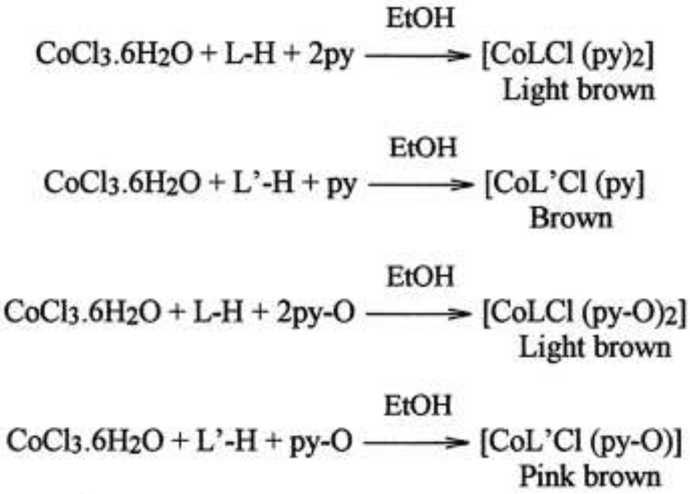
$$CoCl_3.6H_2O + L'\text{-}H \xrightarrow{EtOH} [CoL'X(H_2O)]$$

Reddish yellow

(B) Synthesis of complexes of type [MLXB2] and [ML'XB]

Where, X = Cl and B = Pyridine (-py) and Pyridine-N-oxide (-py-O)

Aqueous ethanolic metal salt solution (0.021 moles in 40 mL of aq. ethanol) was mixed with ethanolic solution of the ligand (0.02 moles in 50 mL) and warmed with base on water-bath. It was further digested for a few minutes and the precipitate was filtered. It was washed with water several times and then with ethanol. It was dried at room temperature. Complexes with other bases were prepared similarly. The complexes obtained were collected for analysis and characterisation.



$$CoCl_3.6H_2O + L\text{-}H + 2py \xrightarrow{EtOH} [CoLCl(py)_2]$$

Light brown

$$CoCl_3.6H_2O + L'\text{-}H + py \xrightarrow{EtOH} [CoL'Cl(py)]$$

Brown

$$CoCl_3.6H_2O + L\text{-}H + 2py\text{-}O \xrightarrow{EtOH} [CoLCl(py\text{-}O)_2]$$

Light brown

$$CoCl_3.6H_2O + L'\text{-}H + py\text{-}O \xrightarrow{EtOH} [CoL'Cl(py\text{-}O)]$$

Pink brown

RESULTS AND DISCUSSION

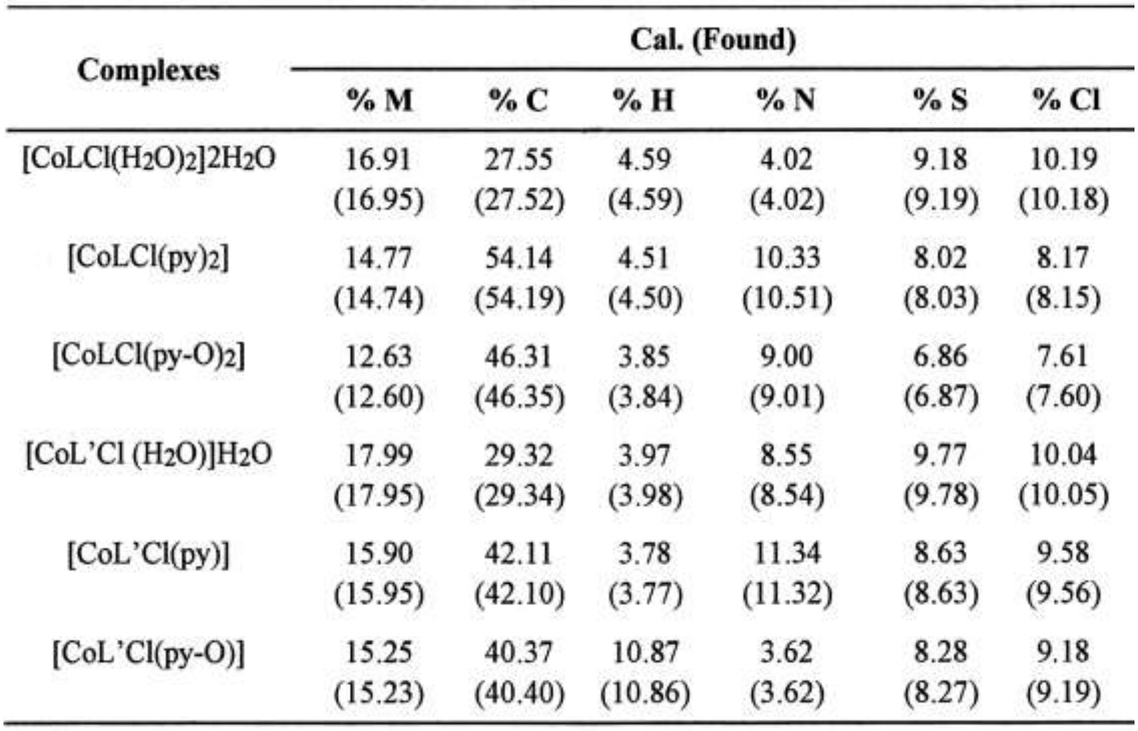
Physico-chemical characterizations and geometrical configuration of the complexes

Co (III) salt reacts with MBAHA-H and AMBAHA-H ligands in 1 : 1 molar ratio in alcoholic medium to afford dark reddish/brown complexes. The ligand and its complexes are stable at room temperature and are non-hygroscopic. The ligands were soluble in common polar organic solvents, such as ethanol, methanol, and chloroform but partially soluble in hexane. The complexes were relatively wellsoluble in DMF and DMSO. The synthesized ligand andits complexes were characterized by elemental analysis, spectra, and molar conductivity measurements. The geometry of the newly synthesized compounds has been elucidated based on their elemental analysis, molar conductivity and spectral data.

Elemental analysis

The stoichiometry of the ligands and their complexes were confirmed by their elemental analysis. The metal/ligand ratio was found to be 1 : 1 has been arrived at by estimating the metal and nitrogen and sulphur contents of the complexes. Elemental analysis of ligands and their Co (III) complexes show good agreement with the proposed structures of the ligands and their complexes Table 1.

Table 1: Analytical table of Cobalt (III) complexes



Complexes	Cal. (Found)					
	% M	% C	% H	% N	% S	% Cl
[CoLCl($(H_2O)_2$)]$2H_2O$	16.91 (16.95)	27.55 (27.52)	4.59 (4.59)	4.02 (4.02)	9.18 (9.19)	10.19 (10.18)
[CoLCl(py)$_2$]	14.77 (14.74)	54.14 (54.19)	4.51 (4.50)	10.33 (10.51)	8.02 (8.03)	8.17 (8.15)
[CoLCl(py-O)$_2$]	12.63 (12.60)	46.31 (46.35)	3.85 (3.84)	9.00 (9.01)	6.86 (6.87)	7.61 (7.60)
[CoL'Cl (H_2O)]H_2O	17.99 (17.95)	29.32 (29.34)	3.97 (3.98)	8.55 (8.54)	9.77 (9.78)	10.04 (10.05)
[CoL'Cl(py)]	15.90 (15.95)	42.11 (42.10)	3.78 (3.77)	11.34 (11.32)	8.63 (8.63)	9.58 (9.56)
[CoL'Cl(py-O)]	15.25 (15.23)	40.37 (40.40)	10.87 (10.86)	3.62 (3.62)	8.28 (8.27)	9.18 (9.19)

Molar conductance measurements

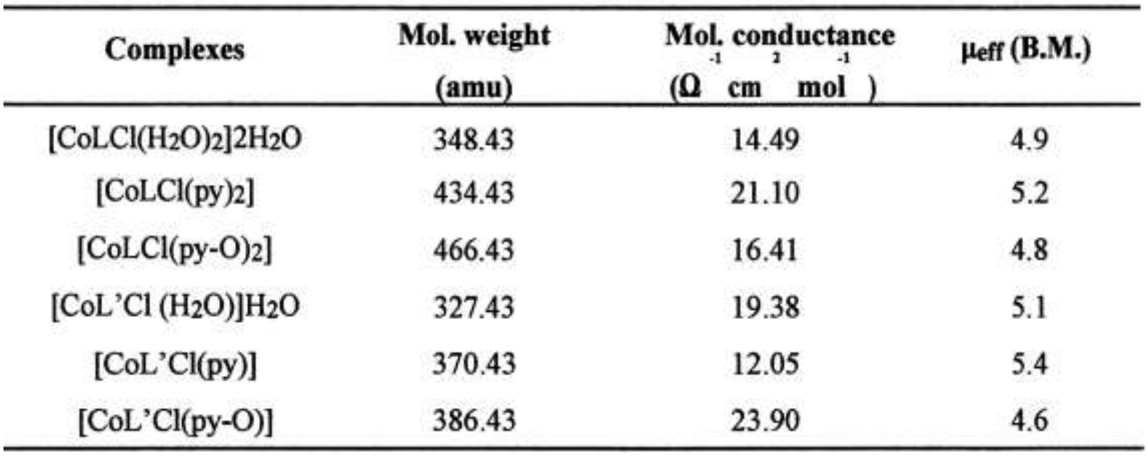
The molar conductance values (14-24 $olun^{-1}cm^{2}mol^{-1}$) of the complexes which were determined in DMSO solvent indicate that the complexes under study are non-electrolytic in nature[15,16] (Table 2).

Magnetic susceptibility measurements

The observed magnetic moments of Co (III) complexes of MBAHA-H and AMBAHA-H are given in Table 2. The theory of magnetic susceptibility of cobalt (III) ion was given originally by Schalp and Penny[17] and the best results on the magnetic behaviour of cobalt complexes is that of Figgis and Nyholm[18]. The observed values of magnetic moment for Co (III) complexes are generally diagnostic of the coordination about the metal ion.

The magnetic measurements on the complexes reported herein show that all were paramagnetic and have three unpaired electrons indicating high-spin octahedral stereo-chemistry. For the present complexes these values lie in the range 4.6 to 5.4 B.M.

Table 2: Physical properties of Cobalt (III) complexes



Complexes	Mol. weight (amu)	Mol. conductance (Ω^{-1} cm^{2} mol^{-1})	μ_{eff} (B.M.)
$[CoLCl(H_2O)_2]2H_2O$	348.43	14.49	4.9
$[CoLCl(py)_2]$	434.43	21.10	5.2
$[CoLCl(py\text{-}O)_2]$	466.43	16.41	4.8
$[CoL'Cl\ (H_2O)]H_2O$	327.43	19.38	5.1
$[CoL'Cl(py)]$	370.43	12.05	5.4
$[CoL'Cl(py\text{-}O)]$	386.43	23.90	4.6

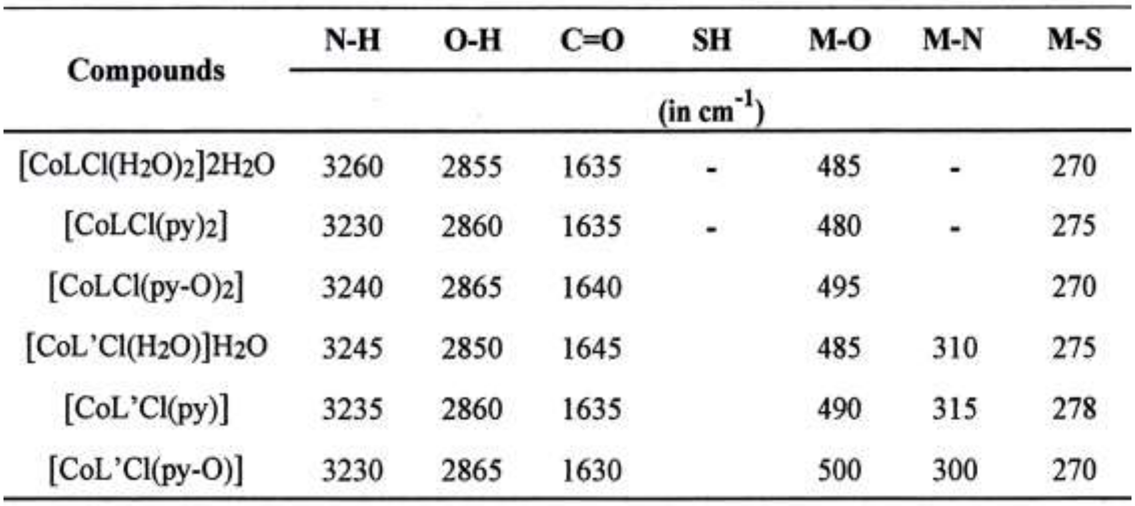
IR spectral studies

The structural possibilities of the complexes depend upon the mode of coordination of the ligands. The IR spectral studies are quite useful on determining the mode coordination of ligands. On critically examining the position and direction of the shifts of the frequencies of the ligands in the complexes, as compared to their positions in the freestate, the mode of coordination can be suggested for all the investigated complexes.

The IR spectral studies show that the ligand MBAHA-H acts as mono negative tridentate (SOO' donor) ligand but AMBAHA-H acts as mono negative tetra dentate (SOO'N donor) ligand. The ligand MBAHA-H coordinating with metals through thioalcoholic S, carbonyl 0 and hydroxamic 0 atoms respectively [Fig. 1] and the ligand AMBAHA-H coordinating with metals through thioalcoholic S, carbonyl O hydroxamic O atoms and primary amino N atoms respectively (Fig. 2). The main infrared bands and their assignments are presented here in Table 3.

The band at 3275 cm^{-1} due to v (N-H) mode remains intact in complexes indicating the non participation of N-H group of hydroxamic acid in coordination with the metal ion. The IR spectra of ligands showed a medium intensity band at 2570 cm^{-1} for v (S-H). The absence of this band in complexes indicates the destruction of the S-H bonding followed by complexation of S with Co (III) ion after deprotonation19. This is further supported by a downward shift in v (C-S) by 15-25 cm^{-1} in the complexes and the disappearance of a low intensity band at 275-295 cm^{1} due to M-S stretches. The v (C=0) stretch shifts to lower in the complexes by 15-25 cm^{1}, suggesting involvement of carbonyl oxygen in coordination". This is further supported by the appearance of new low intensity bands around 450-500 cm-1 in the spectra complexes due to the v (M-O) stretch. The v (0-H) stretch shifted to lower frequency in the complexes by 20-30cm^{1} suggesting coordination of hydroxamic acid group through deprotonated O-H group with metal[19]. The medium and sharp band located at 1300 cm-1 in theligand attributed due to the deformation vibration of alcoholic v (OH) disappears in all the complexes suggesting the deprotonation of the alcoholic OH and coordination of alcoholic O to the metal ion. This is further supported by the appearance of new low intensity bands around 420-465 cm^{-1} in the spectra complexes due to the v (M-O) stretch. Further, the 1R spectra of complexes with AMBAHA-H ligand showed the band attributed to v (NH_2) of the coordinated amino group, which appeared at iv 50 cm^{-1} than in the spectrum of ligand (a medium intensity band around 1525-1535 cm^{1}).

Table 3: Important I.R. bands of ligands and Co (III) complexes



Compounds	N-H	O-H	C=O	SH	M-O	M-N	M-S
				(in cm^{-1})			
$[CoLCl(H_2O)_2]2H_2O$	3260	2855	1635	-	485	-	270
$[CoLCl(py)_2]$	3230	2860	1635	-	480	-	275
$[CoLCl(py\text{-}O)_2]$	3240	2865	1640		495		270
$[CoL'Cl(H_2O)]H_2O$	3245	2850	1645		485	310	275
$[CoL'Cl(py)]$	3235	2860	1635		490	315	278
$[CoL'Cl(py\text{-}O)]$	3230	2865	1630		500	300	270

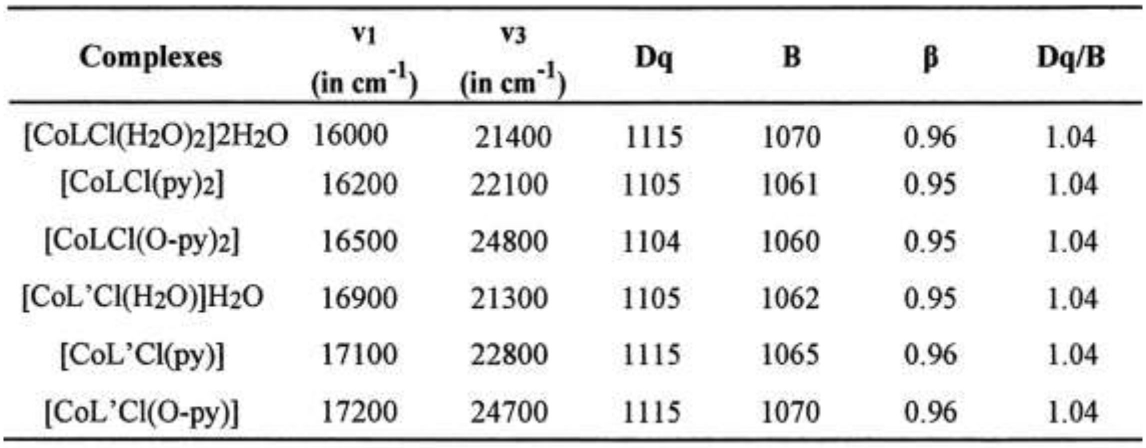
In case of aqua-complexes the appearance of one more band in the range of 750-850 cm^{-1} due to rocking and wagging mode of vibrations indicated that water (H_2O) was present in the coordination sphere. The coordination through N donor monodentate ligands, e.g. pyridine and different picolines have been further confirmed by the appearance of v (M-N) band at 455-535 cm^{-1}. The appearance of a low intensity band around 220-230 cm^{-1} in some complexes indicated the coordination of Cl with the Co (III) [v(M-C1)].

Electronic spectral studies

The study of magnetic and electronic spectra data is quite informative in characterizing the geometry of the complexes. The UV-visible spectrum of the ligands and their complexes were recorded in DMSO solution.

The electronic spectra of all the complexes recorded herein are very similar with each other and consist of two bands, one in the 17240-16630 cm^{-1} and the other in 22000-20420cm^{-1} regions, which clearly indicated the high-spin octahedral stereochemistry of the complexes that was confirmed by the observed magnetic moment values (4.6 to 5.4 B.M). The monomeric nature of the complexes was confirmed by their magnetic moment values. In Table 4, the band maxima and their assignments and the calculated ligand field parameters are listed.

Table 4: Electronic spectral bands (cm^{-1}) and ligand field parameters of Co (III) complexes of MBAHA and AMBAHA



Complexes	ν_1 (in cm^{-1})	ν_3 (in cm^{-1})	Dq	B	β	Dq/B
$[CoLCl(H_2O)_2]2H_2O$	16000	21400	1115	1070	0.96	1.04
$[CoLCl(py)_2]$	16200	22100	1105	1061	0.95	1.04
$[CoLCl(O\text{-}py)_2]$	16500	24800	1104	1060	0.95	1.04
$[CoL'Cl(H_2O)]H_2O$	16900	21300	1105	1062	0.95	1.04
$[CoL'Cl(py)]$	17100	22800	1115	1065	0.96	1.04
$[CoL'Cl(O\text{-}py)]$	17200	24700	1115	1070	0.96	1.04

When all the bands, v_1, v_2, and v_3 are observed to be free from shoulders, the ligand field parameters Dq and B are in principle calculated using first order perturbation theory and the transition energies are given by the following equations:

$$V_1 = 5\ Dq - 7.5\ B + \tfrac{1}{2}\ (225\ B^2 + 100\ Dq^2 + 180\ DqB)^{1/2}\ V2 = 15\ Dq — 7.5B +'/2\ (225\ B^2 +$$

$$100\ Dq^2 + 180\ DqB)^{1/2}\ V_3 = (225\ B^2 + 100\ Dq + 180\ Dq\ B)^{1/2}$$

The methods of calculation of ligand field parameters from the ligand field spectra of octahedral Co (III) complexes have been discussed by Reedijk[21]. The existence of distortion from a regular octahedral structure is revealed in all the Co (III) complexes studied herein by appreciable intensity enhancement.

On the basis of the forgoing evidences, the proposed octahedral geometry i.e., Oh symmetry for the complexes is presented in Fig. 2 and 3.

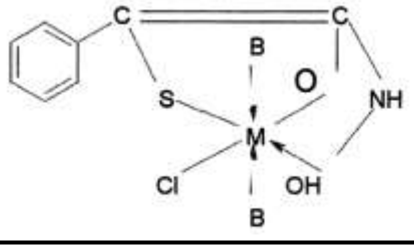


Fig. 2: Proposed octahedral structure complexes of Co (III) with MBAHA-H ligand (B = Monodentate secondary ligands)

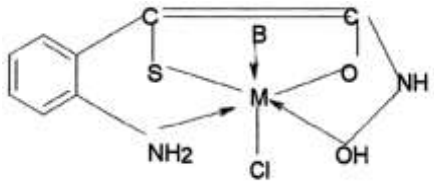


Fig. 3: Proposed octahedral structure complexesof Co (III) with AMBAHA-H ligand (B = Monodentate secondary ligands)

CONCLUSION

Six complexes of the ligands MBAHA-Hand AMBAHA-H with Co^{3+} have been synthesized and characterized. The IR spectral studies revealed that the ligands MBAHA-H and AMBAHA-H acted as a mononegative tridentate (S00 donor) and tetradentate (SOON donor), respectively in all the complexes. The magnetic, conductance and electronic spectral studies revealed that the complexes were paramagnetic with octahedral geometries. All the investigated complexes were non-electrolyte and monomer.

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