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Physico Chemical character of the complexes prepared with Mn (II) by using 5-Mercapto-4-amino-3-Methyl-1,2,4-Triazole as Ligand

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ARTICLE DETAILS

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ABSTRACT

The complexes prepared with Mn(II) by using 5-Mercapto-4-amino-3-Methyl-1,2,4-Triazole have been prepared and characterised using various physico-chemical studies. The structure of the complexes are assigned using IR, megnetic moment and other physicochemical measurements.

1. Introduction

Manganese is essential for normal bone structure reproduction and normal functioning of the central nervous system, Pyruvate Carboxylase and Superoxide dismutase contains tightly bonded mangnese. Mangnese ions activate glyesyltransterase, which is concerned with the synthesis o the mncopolysachhrides of Cartilage and associated with the synthesis of glycol protein.[1] It activates is clitrate dehydrogenase and phosphotransference. Arginase is activated by mangnese ions. Mangnese ion inhibits lipid per oxidation reaction. Mangnese ion act as cofactor along with glucose-6-phosphate dehydrogenase.

2. Preparation of Complexes

(i) Mn (II) complexes with 4-amino-5-mercapto-3-methyl-1,2,3,-triazole in acidic medium at pH=4

About 0.01 mole of $MnCl_2.6H_2O$ was dissolved in distilled water and the solution was filtered in hot condition. About 0.1 mole of ligand was dissolved in hot aqueous ethanol and mixed in hot condition and pH of mixed solution was adjusted to ~ 4 by adding a few drop of HCL. The mixture was digested and refluxed over water bath for one hour when dull white precipitate of the complex was obtained. The precipitate was filtered and washed by hot water, ethanol and ether. It was then dried over anhydrous $CaCl_2$ in a vacuum desiccator.

3. Experimental

Elemental analysis

Element	%found
C	16.90
H	3.52
N	26.25
CL	16.60
S	15.01
Mn	12.82

On the basis of elemental analysis expected empirical formula of the Complex will be $Mn(C_6H_{16}S_2O_2Cl_2)$. This complex is represented by molecular formula $Mn(LH)_2(H_2O)_2Cl_2$...(A1). The complex requires.

Element	% Calculated
C	17.06
H	3.79
N	26.54
CL	16.82
S	15.16
Mn	13.03

Calculated Molecular Weight =422
Magnetic moment μ_{eff} = 5.92BM

(ii) Mn (II) complexes with 4-amino-5-mercapto-3-methyl-1,2,3,-triazole in neutral medium (pH=7)

About 0.01 mole of hydrated $MnCl_2$ dissolved in distilled water and the solution was filtered in hot condition. Now 1:2 molar proportion of ligand dissolved in 50 ml hot ethanol was mixed in hot condition and the pH of solution was adjusted to 7 by adding a few drop of NH_4OH. The mixture was digested and refluxed over water bath for one hour when cream white complex separated. The precipitate of the complex obtained was filtered and washed by hot water, ethanol and ether. It was hen dried over anhydrous $CaCl_2$ in vaccum disiccator.

Elemental analysis

Element	% Found
C	18.49
H	4.58
N	28.61
Mn	14.18

On the basis of elemental analysis empirical formula of complex will be $Mn(C_3H_5N_4S)_24H_2O$. The elemental content of complex on calculation requires:

Element	% Found
C	18.70
H	4.67
N	29.09
Mn	14.28

This Complex is represented by symbol A_2
Calculated Molecular Weight=385
The magnetic moment value was found
μ_{eff} = 5.93 BM at 303^0K
Colour of Complex = Cream White

(iii) Mn(II) complex with 4-amino-5-mercapto-3-methyl-1,2,3,-triazole in basic medium pH=10

About 0.01 mole of hydrated $MnCl_2$ was dissolved in water and the solution was filtered in hot condition. Now the hot ethanolic solution of 0.1 mole of ligand was mixed in hot condition and the pH of solution was adjusted to ten. The mixture was digested and refluxed on a steam bath for two hours. When dirty white coloured precipitate of complex was obtained. The obtained precipitate was filtered and washed by hot water, ethanol and ether. It was then dried over anhyrous $CaCl_2$ in vacuum desiccator.

Elemental analysis :

Element	**%found**
C	12.13
H	5.68
N	19.21
Mn	18.78

The analytical result of complex correspond to formula $MnL(OH).5H_2O$. The complex requires :

Element	**% Calculated**
C	12.37
H	5.49
N	19.24
Mn	18.90

This Complex is represented by symbol A_3
Calculated Molecular Weight=291
The magnetic moment value was found
$\mu_{eff} = 5.95$
Colour of Complex = Dirty White

MAGNETIC MOMENT MEASUREMENT

Complexes		**Magnetic Moment (BM)**
A_1	$[Mn(LH)_2(H_2O)_2]Cl_2$	5.92
A_2	$[MnL_2(H_2O)_2]H_2O$	5.93
A_3	$[MnL(OH)(H_2O)_3]2H_2O$	5.95

Magnetic moment measurements of each complex indicates that they are paramagnetic. The magnetic moment value of a complexes occur in normal range of octahedral environment of ligand around metal atom.

4. Results and discussion

From the results of elemental analysis, it has been found that Mn(II) form complexes of composition $Mn(LH)_2Cl_22H_2O$, MnL_24H_2O and $MnL(OH)5H_2O$. Mn(II) complexes are obtained as stable chelate and these are dirty brown or light cream coloured product. The complexes are almost insoluble in water but dissolve slighty in hot ethanol. All Mn(II) complexes are soluble in dimethylformamide (DMF). The DMF solution of $MnL(OH)5H_2O$ and MnL_24H_2O are almost no conducting (λ_α ~ 5-10 Ohm^{-1} $mole_{-1}$ cm^2) indicating their non-ionic character. The electrical conductance value of complex $[Mn(LH)_2(H_2O)_2]Cl_2$ was ~ 156 Ohm^{-1} mol^{-1} d cm^2 in DMF solution at 30°C. The electrical conductance value of complex $Mn(LH_2)(H_2O)_2Cl_2$ indicated its ionic nature and complex is 1:2 electrolyte. The complex $Mn(LH)_2Cl_22H_2O$ on heating do not loss weight below 130-140°C. On heating the complex above 160°C, slowly starts losing weight and it starts decomposing above 260°C. This indicated that H_2O is coordinated to Manganese(II) in complex $[Mn(LH)_2(H_2O)_2]Cl_2$. The neutral complex MnL_24H_2O starts losing weight above 40°C and losses two water molecules at 90-95°C. After heating the complex, the weight is constant upto 150°C. The complex then start decomposing above 250°C. This indicated that complex MnL_24H_2O has two coordinated water and two molecules of water is present as water of crystalisation. In case of complex $MnL(OH)5H_2O$, the complex losses three water molecule below 90°C on heating and ten decomposes slowly above 140°C. All the complexes of Managnese(II) are paramagnetic and magnetic moment value complexes was found between 5.95-5.92 BM. suggesting oxidation state two and have five unpaired spin. The magnetic moment value of complexes occur in the range of six coordinated octahedral structure. The electronic absorption spectrum of complex do not display distinct band in visible region 380-750 nm. The complexes display electronic bands associated with ligand molecule at 240, 295 and 325 nm. These electronic bands are located at 235, 290 and 320 nm in free ligand. The slight change in electronic band is due to coordination of ligand molecule and these electronic transitions are assigned to $\sigma-\pi^{\times},\pi-\pi^{\times}$ and $n-\pi^{\times}$ transition present in ligand molecule. The Mn(II) has d^5 electronic system and its ground state has ^6s configuration and excited state has quarterate state $^4T_{1g}$ and $^4T_{2g}$. As no spin allowed transitions are present, hence no distinct electronic band is expected in Mn^{2+} complexes.

Comparison of I.R. spectra of the Ligand and complexes of Mn^{+2} salts formed by the Ligand

Table – 3
Wave Numbers (Cm–1)

Compound	**ν(H_2O)**	**ν(NH_2)** ν(N-H)	**ν(S-H)**	**ν(C-N)** δ(NH2)	**Thioamide Band**				**δ(CH_3)**	**P(H_2O)**
					I	**II**	**III**	**IV**		
Ligand	---	3260 3210(S) 3110(m) 3050(m)	2450	1215(m) 1100(m)	1570	1390 1380	1080	780	1480 1450	--
A_1	3600 W 3542 S 3448 S 3585 S	3250 3200 (S) 3100 (S) 3040 (W)	--	1260 1750	1500	1340	1070 W	667	1480 1450	630

A_2 **Anhydrous compounds**	3600 W 3542 S 3440 S 3580 S	3250 3200 (S) 3100 (S) 3040 (W)	--	1260 1170	1520	1340	1065	667	1480 1450	653
A_3	3600 3542 s 3440 (s) 3580 (s)	--	--	1260 1170	1490	1320	1060	710	1480 1450	635

Interpretation of I.R. spectra of the complexes of Mn+2 formed by the Ligand

A comparison of I.R. spectra of Ligand and the complexes A_1, A_2 & A_3 indicates that–

(1) There are strong broad bands in the region of 3600-3580 cm–1. The bands are assigned to combination of νNH_2, $\nu(NH)$ and νH_2O mode of vibration with hydrogen boding.

(2) The additional band at 1640 cm^{-1} and 650 cm^{-1} indicates the δH_2O & ρH_2O mode of vibration.

These observations are in good agreement of presence of water molecules in the hydrated complexes.

(3) Thioamide band (I) is observed at 1500 cm^{-1} in A_1 at 1520 in A_2 and 1490 cm^{-1} for A_3. A red shift (50-80cm^{-1}) with respect to the ligand molecule in all complexes indicates the involvement of thioamide unit in complexation process.

(4) A red shift is also observed in the thioamide band (II) in all complexes.

(5) A red shift is again observed in thioamide band (III). These bands are mainly due to ν(C-N) and ν(C=S) mode of vibrations. This shift again indicates the involvement of sulphur atom in all complexes of Mn(II).

(6) The bands at 2450 cm^{-1} observed in free ligand is absent in the complexes which indicated the absence of S-H group in complexes. This indicated that SH is deprotonated in natural complex and the ligand is almost present in thione form in complex $[Mn(LH)_2(H_2O)_2]Cl_2$.

(7) The free ligand display two bands located at 1215 and 1100 cm^{-1} assignable to NH^2 rocking and wagging mode of vibration. In complexes these band shift to higher wave number and observed around 1260 and 1160-1170 cm^{-1}. The shift of rocking and scissoring mode of i.r. vibration of ligand in complexes suggested the coordination of amino group NH_2 nitrogen in complexes[12-13].

(8) A weak band at 630 cm^{-1} indicates the presence of rocking mode of H_2O group in complexes.

Hence, by comparing the I.R. data bands of the ligand with those of complexes A_1, A_2 and A_3, we can say that the ligand is coordinated through sulpur atom of thioamide group and nitrogen of NH_2 group.

Thus from the IR-spectral studies and discussion of magnetic moment value, electrical conductance measurement and composition of complexes six coordinated octahedral structure is suggested for all Mn(II) complexes prepared at pH-4, 7 and 10. In case of complexes formed at pH ~ 4 the ligand appears to be bonded as bidentate neutral molecule. At pH-7 the ligand is deprotonated in thiol tautomer and while at pH ~ 10 (basic medium) a hydroxyl group (OH) is bonded to Mn(II) and the ligand is bonded as monoanionic acidic group. Thus the probable structure of Mn(II) $[Mn(LH)_2(H_2O)_2]Cl_2$ (A_1), $[MnL_2(H_2O)2]2H_2O$ (A_2) and $[MnL(OH)(H_2O)_3]H_2O$ (A_3) are given below in figure X, Y and Z respectively.

Structure of Complex A1 = $[Mn(LH)_2(H_2O)_2]Cl_2$

(X) Diaquo bis (4-Amino-5mercapto-3-methyl-1,2,4-triazole) Manganese(II) Chloride

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