Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2011, 2 (2): 125-129

ISSN: 0976-8505
CODEN (USA) CSHIA5

Synthesis and Characterization of Some Acid green-20 dye Complexes of 3d Metal ions and Zn(II)

N. K. Prajapati, Jignesh A. Patel, Janki Vyas*, Asha D. Patel and G. R. Patel**

Department of Chemistry, M.N. College, Visnagar, Dist.: Mehsana, (N.G.), Gujarat, India
**Department of Chemistry, Hemchandracharya North Gujarat University, Patan, Gujarat, India*
***Department of Chemistry, Sheth M.N. Science College, Patan, Dist.: Patan, (N.G.), Gujarat, India*

ABSTRACT

Novel binary complexes of 3d Metal ions and Zn(II) (Mn^{+2},Co^{+2},Ni^{+2},Cu^{+2}) has been synthesized using Acid green-20 [1-2] ligand capable of forming stable chelate. After syntheses the complexes were characterized by chemical as well as instrumental methods. Like elemental, IR, TGA ,Absorption Spectral Data analyses.

Keywords: Acid Green -20 Dye, 3d Metal ions, chelate, IR, Absorption Spectral Data.

INTRODUCTION

Acid dye is a member of a class of dye that is applied from an acidic solution. In the home or art studio, the acid used in the dyebath is often vinegar (acetic acid) or citric acid. The uptake rate of the dye is controlled with the use of sodium chloride[3].

In textiles, acid dyes are effective on protein fibers, i.e. animal hair fibers like wool, alpaca and mohair. They are also effective on silk. They are effective in dyeing the synthetic fiber nylon but of minimal interest in dyeing any other synthetic fibers.

Acid dyes are thought to fix to fibers by hydrogen bonding, Van der Waals forces and ionic bonding. They are normally sold as the Sodium salt therefore they are in solution anionic. Animal protein fibers and synthetic Nylon fibers contain many cationic sites therefore there is an attraction of anionic dye molecule to a cationic site on the fiber. The strength (fastness) of this bond is related to the desire/ chemistry of the dye to remain dissolved in water over fixation to the fiber[2].

MATERIALS AND METHODS

1:1 mole ratio of metal perchlorate {$Mn(ClO_4)_2$, $Co(ClO_4)_2$, $Ni(ClO_4)_2$, $Cu(ClO_4)$, $Zn(ClO_4)$} and dye were taken in the form of aqueous solutions, after mixing, this mixture was refluxed with water condensor for 2 hours at 150□C temperature, until the mixture remains ¼ part. After doing this process the solution was cooled and the binary complex isolated from the mixture, it was cooled, filtered and washed with pure water and alcohol to remove impurities soluble in those solvents, then it was characterized by different methods.

RESULTS AND DISCUSSION

Elemental analysis of the binary complexes isolated in the present study is given in Table: I. The important infrared absorption bands and spectra of dyes and its metal complexes using PERKIN ELMER Spectrophotometer ; Frequency range : 4000 – 450 cm^{-1} (KBr disc.),

Iinfrared spectra of metal complexes exhibit bands corresponding to Acid Green-20 and metal complexes. Bands were obtained in the far IR regionThe IR spectra indicates the presence of Acid Green-20 in the binary complexes. (Table : II) The presence of water molecules in the indicated by broad band around 3400 cm^{-1} and some additional bands at 506 cm^{-1}, 508 cm^{-1}, 532 cm^{-1} and 511 cm^{-1} assigned to M-OH_2 bands.[4] The acid green-20 molecule shows the following characteristic bands : 3373 cm^{-1}(O-H and aromatic C-H stretching), 1219 cm^{-1} (C-O stretching), 1597 and 1567 cm^{-1} (N-H stretching).[5] The usual ring skeleton ϑ(C-C) bands are observed at

1600,1450,1410 and 1345 cm^{-1}.[6] In the metal complexes following bands are in comparison of acid green-20. Metal complex dyes show absorption bands at 3742 cm^{-1} and 3819 cm^{-1} it gives information about primary alcohol.[7-8] Very most important bands are shown by metal complexes at 465,466 and 463 cm^{-1} indicating M-O stretching bands.[9]

The thermograms were analysed to obtain information about the percentage weight loss at different temperatures. It has been observed that M(II) chelates show loss in weight corresponding to two water molecules in all metal complexes of Acid Green 20. (Table-III)

The following important observations have been made :
It has been observed that all the metal complexes shows loss in weight. There are two water molecules of crystallization observed in all metal complexes of Acid Green 20 and one coordination water molecule observed in all metal complexes.

In general, the water of hydration may be considered as either the crystallization water of coordination water. According to Nikolaev et al.[10] water eliminating below 150˚C can be considered as the water of crystallization and water eliminated above 150˚C may be due to its coordination in the metal complex.

Electron Spectra Study : The apperance of two bands in the spectra of the Ni(II) chelate at 16474 cm^{-1} and 22883 cm^{-1} are assigned[12] to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively, suggesting an octahedral geometry for the Ni(II) chelate. The electronic spectral parameters are reported in Table : V

The Co(II) chelate registers an intense bands 18474 cm^{-1} and 22840 cm^{-1}. These may be assigned respectively to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions of a typical octahedral coordinated Co(II) ion.[11] The electronic spectral parameters are reported in Table : V

Table : I. Analytical Data and Some Physical Properties of the Metal Complexes.

Compound Molecular Formula	Colour	Formula Weight	Analysis (%) Calculated / (Found)				M.P. °C
			C	H	N	M	
[Acid Green -20] $C_{22}H_{18}N_6O_7S_2$	Bluish Green	540.52	48.72 (47.19)	2.95 (2.21)	15.49 (14.23)	-	>300
[Mn - (Acid Green -20)· H_2O] ·$2H_2O$ $C_{22}H_{24}N_6O_{10}S_2$ Mn	Light Green	644.94	40.93 (40.07)	3.57 (2.79)	13.02 (12.18)	8.51 (7.27)	>300
[Co - (Acid Green -20)· H_2O] ·$2H_2O$ $C_{22}H_{24}N_6O_{10}S_2$ Co	Greenish Black	648.93	40.68 (40.13)	3.54 (2.81)	12.94 (12.09)	9.08 (8.25)	>300
[Ni - (Acid Green -20)· H_2O] ·$2H_2O$ $C_{22}H_{24}N_6O_{10}S_2$ Ni	Bluish Green	648.69	40.69 (38.97)	3.54 (2.67)	12.95 (11.73)	9.04 (8.07)	>300
[Cu - (Acid Green -20)· H_2O] ·$2H_2O$ $C_{22}H_{24}N_6O_{10}S_2$ Cu	Green	653.55	40.39 (39.33)	3.51 (2.95)	12.95 (11.73)	9.72 (9.05)	>300
[Zn - Acid Green -20] ·$3H_2O$ $C_{22}H_{24}N_6O_{10}S_2$ Zn	Light Green	654.39	40.34 (40.73)	3.51 (3.03)	12.83 (12.01)	9.99 (8.25)	>300

Table : II Infrared Spectra of the Metal Complexes of Acid Green -20 (Cm^{-1})

NO	Compound	ϑ(O-H) ϑ(P-OH)	ϑ (-SO_3H) ϑ (S=O)	ϑ (N-H)	ϑ (C-O)	ϑ (N-r)	ϑ (C-S)	ϑ (Ar(C-H)	ϑ (M-O)	ϑ (M-OH_2)
1	Acid Green – 20	3373	1046	1597 1567	1219	885 830	639	1140 912 752	-------	----------
2	[Mn-(A.G.-20))· H_2O] ·$2H_2O$	3375	1046	1598 1568	1222	884 828	638	1182 912 751	465	507
3	[Co-(A.G.-20))· H_2O] ·$2H_2O$	3370 3819	1047	1598 1567	1222	884 828	638	1140 912 751	466	508
4	[Ni-(A.G.-20))· H_2O] ·$2H_2O$	3742 3344	1043	1598 1549	1292	899 829	627	1142 926 751	463	532
5	[Cu-(A.G.-20))· H_2O] ·$2H_2O$	3419	1065	1539 1507	1211	841	626	1109 939 752	460	511
6	[Zn – A.G.-20] ·$3H_2O$	3375	------	1598 1568	1222	884 829	638	1140 912 751	466	506

N.B : P= Primary Alcohol, N-r= Napthalene Ring, AR-(C-H) = Aromatic (C-H) Banding, A.G.-20= Acid Green -20, All are stretching frequency.

Table : III Water content at 25˚C and cumalative Weight Loss Data of the Metal Chelate at 50˚C, 100˚C and 150˚C

Complex	50˚C		100˚C		150˚C	
	g	%	g	%	g	%
[Mn-(A.G.-20))· H_2O] ·2H_2O	0.595	0.1	47.675	8.0	59.593	10.0
[Co-(A.G.-20))· H_2O] ·2H_2O	0.599	0.1	41.995	7.0	59.99	10.0
[Ni-(A.G.-20))· H_2O] ·2H_2O	0.599	0.1	41.978	7.0	59.369	9.9
[Cu-(A.G.-20))· H_2O] ·2H_2O	0.604	0.1	36.272	6.0	48.363	8.0
[Zn – A.G.-20] ·3H_2O	0.606	0.1	47.904	7.9	54.575	9.0

Table: IV Cummulative % Weight Loss Data of Metal Complexes at Various Temperatures(°C).

Complex	**50°C**	**100°C**	**150°C**	**200°C**	**250°C**	**300°C**	**350°C**	**400°C**	**450°C**	**500°C**	**550°C**	**600°C**
[Mn-(A.G.-20))· H_2O] ·2H_2O	0.1	8.0	10.0	11.0	15.0	19.0	23.0	28.0	33.2	38.0	41.3	43.0
[Co-(A.G.-20))· H_2O] ·2H_2O	0.1	7.0	10.0	11.8	14.0	18.0	22.0	29.9	35.0	38.0	40.0	42.0
[Ni-(A.G.-20))· H_2O] ·2H_2O	0.1	7.0	9.9	12.0	20.0	28.0	34.0	40.0	45.5	49.0	52.0	54.0
[Cu-(A.G.-20))· H_2O] ·2H_2O	0.1	6.0	8.0	10.5	20.0	26.0	32.0	37.0	42.0	45.0	47.0	51.0
[Zn – A.G.-20] ·3H_2O	0.1	7.9	9.0	12.0	12.0	18.0	24.0	32.0	37.0	40.0	44.0	46.0

***N.B** : A.G.-20 = Acid Green -20 Dye*

Table:V Absorption Spectral Data and Magnetic Moment of the Metal Complexes.

Compound	**Transitions**	**Assignment**	μ_{eff}
[Mn - (Acid Green -20)· H_2O] ·2H_2O	19531 22883 26101	$^6A_{1g} \rightarrow {}^4T_{1g}$ $^6A_{1g} \rightarrow {}^4T_{2g}$ $^6A_{1g} \rightarrow {}^4A_{1g}$	5.39
[Co - (Acid Green -20)· H_2O] ·2H_2O	22840 18474	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	**4.16**
[Ni - (Acid Green -20)· H_2O] ·2H_2O	16474 22883	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	**3.16**
[Cu - (Acid Green -20)· H_2O] ·2H_2O	13371 25719	$^2E_g \rightarrow {}^2T_{2g}$ C.T.	**1.87**
[Zn - Acid Green -20] ·3H_2O	**36101** **25510** **22883**	C.T.	**Diamagnetic**

The apperance of three bands in the spectra of the Mn(II) chelate at 19531,22883 cm^{-1} and 26101 cm^{-1} are assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4A_{1g}$ transitions, respectively, suggesting an octahedral geometry for the Mn(II) chelate. The electronic spectral parameters are reported in Table : V

In case of the copper (II) chelate, three transitions bands, $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ are possible in octahedral Cu(II) chelate[13] but only two transitions have been observed at 13371 cm^{-1} and 25719 cm^{-1}. The third band is probably mixed with a ligand metal charge transfer transition. The electron spectra as well as magnetic moment data suggest octahedral geometry for Cu(II) chelate. The electronic spectral paremeters are reported in Table : V

REFERENCES

[1] Physical Properties of acid green-20 http://chemexper.com/acid green-20, **2005**.

[2] Acid dye - Wikipedia, the free encyclopedia. http://en.wikipedia.org/wiki/Acid dye, **Aug-2008.**
[3] "Dye Introduction" - Wikipedia, the free encyclopedia.**Aug-2008.**
[4] Patel G.P.; Sharma S.S.; Vora J.J.; and Joshi J.D., *Synth. React. Met.-Org. Chem*., **2002,** 32(10), 1742-1792**.**
[5] Pretsch, E.; Buhlmann P. and Affolter C., "Structure determination of organic compounds" Springer-Verlag Berlin Heidelberg., New York, **2000,** 258,263,264.
[6] Karitzky A.R. and Jones R.A., *J. Chem. Soc.*, **1960**, 2942.
[7] Williams D. and Fleming I., " Spectroscopic methods in organic chemistry", 4th Ed., Tata McGraw Hill; New Delhi, **1998**, 42-58
[8] Jagmohan " Organic spectroscopy- principles and Applications", Narosa Publication House, New delhi, **2001**, p-81.
[9] Kazuo Nakamoto " Infrared and Raman spectra of Inorganic and Coordianation Compounds" 4th Ed. John Wiley and Sons, New York, **1986**, P-229.
[10] Nikolaev A.V., Logavienenko V.A. and Myachina L.I., "Thermal Analysis", Academic Press (New York), **1969**,Vol. 2, p-779.
[11] Jadegoud Y., Ijare O.B., Mallikarjuna N.N., Angagi S.D. and Mruthyunjayaswami B. H, *J.Ind. Chem. Soc*., **2002**, 79, 921-924.
[12] Natarajan C. Sheela C.D. and Athappan D.R**,** *Ind.J.Chem***., 1990**, 29A, 567.
[13] Lever A.B.P., " Inorganic Electronic Spectroscopy", Elsevier, New York, 2nd Ed., **1968,** 355-366.