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MICROWAVE SYNTHESIS, CHARACTERIZATION AND ACOUSTICAL STUDIES OF SOME 3d METAL COMPLEXES CONTAINING 2 ACETYL NAPHTHALENE

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Abstract

Microwave synthesis is a branch of green chemistry. Microwave synthesis has gaind much attention in recent years. The applications of microwave irradiation are used for carrying out chemical transformations, which are pollution free, eco-friendly, low cost and offer high yields together with simplicity in processing and handling. Some new schiff base metal complexes of Co(II), Ni(II) and Cu(II) derived from 2 Acetyl naphthalene with 2-amino phenol (ANAP) and 2-aminothiazole (ANAT) have been synthesized and characterized by various physicochemical methods viz. micro-analytical data, UV-VIS, FT-IR, ESR Spectroscopy molar conductance and magnetic susceptibility measurements. The complexes are colored and stable in air.

Keywords: Microwave Synthesis, IR, UV-Vis, ESR and Acoustical studies.

Introduction

Metal complexes of Schiff bases containing nitrogen and sulpher as donor ligand atoms are of interest in different field like industry, pharmacy and biology.[1-14] Preparation of the new ligands is perhaps the most important step in the development of metal complexes, which exhibit unique desired properties and novel reactivity. Such ligands and their metal complexes have a variety of applications in biology and industry due to their role in catalysis with inorganic & organic synthesis.[15-30] In present paper, the synthesis and characterization of the complexes of Co(II), Ni(II) and Cu(II) involving the Schiff base ligands derived from 2 Acetyl naphthalene with 2-amino phenol (ANAP) and 2-aminothiazole (ANAT) have been reported.

Experimental

All the used chemicals and solvents were of A.R. grade. All the reagents used for the preparation of the Schiff bases were obtained from Sigma Aldrich. Electronic spectra in ethanol were recorded on Perkin Elmer Lambda-2B-spectrophotometer. Molar conductance measurements were conducted using 10^{-3} M solutions of the complexes in ethanol on Elico-CM 82 Conductivity Bridge at room temperature. Magnetic susceptibility measurements were carried out on a Gouy balance at room temperature using $CuSO_4$ as the calibrant. FT-IR spectra were recorded in KBr medium on a Perkin Elmer RX1 spectrophotometer in wave number region 4000-400 cm^{-1}.

Conventional synthesis of Schiff Bases

ANAP and ANAT Schiff bases were synthesized by the condensation of equimolar ratio of 2 Acetyl naphthalene with 2-amino phenol (ANAP) and 2-aminothiazole (ANAT) dissolved in ethanol. The resulting reaction mixture was stirred well, refluxed for 4-6 h and then allowed to cool overnight. The coloured solid precipitate of Schiff base obtained was filtered, washed with cold ethanol and dried in air at room temperature and finally stored under reduced pressure in a $CaCl_2$ desiccators. The purity of synthesized compounds was checked by TLC using silica gel G (Yield: ANAP = 80.40% and ANAT = 80.12%).

Microwave method for the synthesis of Schiff bases

The equimolar(1:1) ratio of 2 Acetyl naphthalene with 2-amino phenol (ANAP) and 2-aminothiazole were mixed thoroughly in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 4-5 ml solvent. The reaction was completed in a short time (5-6 min) with higher yields. The resulting product was the recrystallized with ethanol and finally dried under reduced pressure over anhydrous CaCl2 in a dedicator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G. (Yield: ANAP = 87.40% and ANAT = 89.12%).

Conventional synthesis of Metal Complexes

The metal complexes were prepared by the mixing of (50 ml) ethanol solution of $CoCl_2.6H_2O$/$NiCl_2.6H_2O$/$CuCl_2.2H_2O$ with the (50 ml) ethanol solution of Schiff bases (ANAP/ANAT) in 1:2 (metal:ligand) ratio. The resulting mixture was refluxed on water bath for 6-8 h. A coloured product appeared on standing and cooling the above solution. The precipitated complexes was filtered washed with ether and recrystallized with ethanol several times and dried under the reduced pressure over anhydrous $CaCl_2$ in a desiccator. It was further dried in electric oven at 60-70 °C.

Microwave synthesis of Metal Complexes

The ligand and the metal salts were mixed in 1:2 (metal:ligand) ratio in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 4-5 ml solvent. The reaction was completed in a short time (5-6 min) with higher yields. The resulting product was the recrystallized with ethanol and finally dried under reduced pressure over anhydrous CaCl2 in a desicator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G.

Results and discussion

All the metal complexes are coloured, solid and stable towards air and moisture at room temperature. They decompose on heating at high temperature, more or less soluble in common organic solvents. Analytical data of the compounds, together with their physical properties are consistent with proposed molecular formula are given in **Table 1**. All the metal chelates have 1:1 or 1:2 (metal:ligand) stoichiometry. The observed molar conductance value of the complexes in methanol at room temperature is consistent with the non-electrolytic nature of the complexes. The IR spectra of the ligand (Schiff base) exhibitsa band at 1610 cm^{-1} due to the azomethine (C=N) group. This band shifts to lower frequency by 20-30 cm^{-1} in the complexes showing its participation in chelation through the azomethine nitrogen. The lowering is due to the reduction of electron density in the azomethine link. A sharp band at 830 cm^{-1} is due to C-S-C group. Its position in the complexes has been observed at 821$\pm$6 cm^{-1} indicating the involvement of ring sulphur atom in coordination. An intense band at 1570 cm^{-1} due to C=N cyclic of thiazole ring does not shift in the spectra of complexes. This rules out the participation of (C=N cyclic) group in coordination. Thus the Schiff base acts as bidentate ligand. The appearance of bands at 3310$\pm$5 cm^{-1} (stretching mode) supports the presence of water molecules in all the three complexes. The new bands at 510$\pm$2 cm^{-1} and 470$\pm$7 cm^{-1} has been assigned to M-O and M-N vibration in the complexes.IR data suggest that metal coordinates through N & S donor atoms of Schiff base. This results a four membered metal coordinated ring structure. In literature, based on the experimental data, there are several references where such four membered ring structure have been observed and proposed. However, these may not be considered much more stable . Copper (II) complex, a single broad band at 13695 cm^{-1} has been observed; this attributes to ^{2}Eg-$^{2}T_{2}g$ transition. The various ligand field parameters viz. 10Dq, and LFSE have been calculated and values are 13695 cm^{-1}, (-) 750 cm^{-1} and 98.2 kJ mol^{-1} respectively. Its magnetic moment is 1.90 B.M. Thus these data suggest the octahedral geometry for Cu(II)-complex ligand field parameters and magnetic moment data substantiate the same view. Values of ultrasonic velocity are comparatively higher for the

cupper metal complexes. The values of ultrasonic velocity of various Schiff base (ligand) systems at three different concentrations. Ultrasonic velocity and density decrease on lowering the concentration. With increase the concentration of solution, the ultrasonic velocity (U), acoustic impedance (Z) and molar sound velocity (R) increase while compressibility and intermolecular free length decrease. The increase and decrease of βs values may be ascribed to two effects: (1) the decrease in compressibility caused by the introduction of in-compressible molecules or ions and (2) the addition of solute or compound affects the structure of solvent which results in an increase in compressibility.

Table 1. The comparative results of conventional and microwave methods, analytical and physical data of the compounds.

Compounds Molecular Wt (Colour)	Reaction period		Yield (%)		Elemental Analysis Found/(Calcd.)%				
	CM (h)	MM (Min)	CM	MM	C	H	N	M	Λ_M
ANAP ($C_{18}H_{15}NO$) 261.33 Brown	6.1	5.4	70.2	89.1	47.5 (47.8)	2.5 (2.8)	4.1 (4.3)	-	-
[Co($C_{18}H_{15}NO)_2$ ($H_2O)_3$] 760.59 Blakish green	7.2	6.2	69.1	80.6	35.2 (35.7)	2.7 (3.0)	3.1 (3.2)	13.0 (13.5)	18.9
[Ni ($C_{18}H_{15}NO)_2$ (H_2O)] 760.37 Yellowish green	6.1	6.2	68.3	79.1	35.3 (35.7)	2.5 (3.0)	3.2 (3.2)	13.1 (13.4)	14.5
[Cu($C_{18}H_{15}NO)_2$ (H_2O)] 693.14 Black	6.1	6.2	69.2	78.2	38.2 (38.5)	2.0 (2.2)	3.1 (3.5)	15.3 (15.7)	9.6
ANAT ($C_{15}H_{12}N_2S$) 252.2 Orange	6.1	5.4	70.2	89.1	51.8 (51.9)	3.0 (3.1)	8.0 (8.1)	-	-
[Co($C_{15}H_{12}N_2S$) $_2$ ($H_2O)_2$]Cl_2	6.3	6.1	61.1	69.90	45.6 (45.8	2.9 (3.0)	7.2 (7.1)	7.0 (7.4)	11.2
[Ni($C_{15}H_{12}N_2S$) $_2$ ($H_2O)_2$]Cl_2	6.2	6.1	60.2	69.50	45.5 (45.8)	2.9 (3.0)	6.9 (7.1)	7.2 (7.4)	12.5
[Cu($C_{10}H_{07}BrN_2OS$) $_2$ ($H_2O)_2$]	6.1	6.0	70.2	79.70	45.2 (45.4)	3.0 (3.1)	6.7 (7.1)	7.3 (8.1)	9.4

*Λ_M = (ohm^{-1} cm^2 mol^{-1})

Table 2: Value of density, ultrasonic velocity, apparent molar volume, acoustic impedance), adiabatic compressibility, Rao's Constant, and intermolecular free length, for ligands ANAP & ANAT with metal (Co^{II}/Ni^{II}/Cu^{II}) chlorides and their metal complexes at 301.15K.

Molar Conc. dm^{-3}	$d_o x10^{-3}$ (kgm^{-3})	U (ms^{-1})	$\square_v X10^5$ (m^3mol^{-1})	$Zx10^{-3}$ ($kgm^{-2}s^{-1}$)	$\beta_s X10^{11}$ (m^2N^{-1})	($Rx10^6$)	Sn
ANAP (Ligand)							
0.01	0.8147	1141	484	936.17	80.50	2555.0	163.55
0.005	0.8141	1140	590	929.50	80.51	2553.13	321.66
0.0025	0.8140	1138	705	928.30	80.55	2551.07	593.70
Co(II) – ANAP							
0.01	0.8156	1173	553	957.54	81.66	5977.28	169.73
0.005	0.8154	1173	833	954.53	81.72	5972.50	342.60
0.0025	0.8152	1171	1011	953.47	81.78	59.68.32	634.86
Ni(II) – ANAP							
0.01	0.8160	1177	533	962.24	81.64	5982.99	175.36
0.005	0.8159	1175	780	960.38	81.67	5980.12	340.37
0.0025	0.8156	1173	1016	958.64	81.73	5978.14	656.67
Cu(II) – ANAP							
0.01	0.8160	1182	524	963.11	81.61	6027.80	177.47
0.005	0.8159	1175	829	955.35	81.63	6014.67	348.46
0.0025	0.8156	1171	971	951.01	81.68	6007.82	643.73
ANAT (Ligand)							
0.01	0.8148	1142	485	936.17	80.50	2555.0	163.59
0.005	0.8142	1140	590	929.50	80.52	2554.13	321.69
0.0025	0.8140	1139	706	927.30	80.58	2551.08	593.71
Co(II) – ANAT							

0.01	0.8157	1174	554	957.56	81.66	5977.28	169.73
0.005	0.8155	1172	834	954.53	81.72	5972.50	342.60
0.0025	0.8153	1170	1012	953.48	81.78	59.68.32	634.86
Ni(II) – ANAT							
0.01	0.8160	1177	533	962.24	81.64	5982.99	175.36
0.005	0.8159	1175	780	960.38	81.67	5980.12	340.37
0.0025	0.8156	1173	1016	958.64	81.73	5978.14	656.67
Cu(II) – ANAT							
0.01	0.8160	1182	524	963.11	81.61	6027.80	177.47
0.005	0.8159	1175	829	955.35	81.63	6014.67	348.46
0.0025	0.8156	1171	971	951.01	81.68	6007.82	643.73

ESR spectra: The ESR spectra of Cu(II) provide information about the extent of the delocalization of unpaired electron. The X-band ESR spectra of Cu(II) complexes were recorded in the solid state at room temperature and their $g_{\parallel}$, $g^{\perp}$, Δg, g_{av} and G have been calculated. The values of ESR parameters $g_{\parallel}$, $g^{\perp}$, g_{av}, Δg and G for Cu(II) complex of ANAP &ANAT are 2.199, 2.101, 2.021, 2.012 and 2.526 respectively. The $g_{\parallel}>2.3$ is characteristic of an ionic environment and $g_{\parallel}<2.3$ indicates a covalent environment in metal ligand bonding. The $g_{\parallel}$ values for the complexes are less than 2..3 suggesting, the environment is covalent.

Conclusion

In the present research studies, our efforts are synthesized of some newly compounds. These synthesized compounds characterized by various physicochemical and spectral analyses. The IR data of both the Schiff base and its metal complexes show that the ANAP & ANAT Schiff base is coordinated to the metal ion in tridentate manner with ONO donor sites. FAB-mass data shows degradation pattern of the complexes.

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