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Thermal and Thermotechnical parameters of Co(II), Ni(II), Cu(II) and Zn(II) Metal Complexes of 2-hydroxy-5-methyl-3-nitroacetophenone Schiff base.

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Abstract: A newly synthesized 2-hydroxy-5-methyl-3-nitro acetophenone thiazole Schiff base ligand was derived from the condensation of 2-hydroxy-5-methyl-3-nitro acetophenone and thiazole. The Schiff bases behaved as charge bidentade ligand. The ligand was characterized by elemental analysis and spectral methods. The coordinating ability of the ligand is investigated by preparing its metal complexes with Co(II), Ni(II), Cu(II) and Zn(II) have been prepared and characterized by elemental analysis, conductance measurements, molecular weight determinations, spectral and thermal studies. The Schiff base and their metal complexes have been evaluated for their antibacterial activities The synthesized products are coloured solids, soluble in DMF, DMSO and THF.

Keywords: Schiff base, Magnetic susceptibility, Thermal.

INTRODUCTION

Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules[1]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications[2]. Schiff bases metal complexes have many applications in different fields. The Schiff bases derived from thiazole and substituted acetophenone have been widely used as ligand for the synthesis of transition metal complexes. Thiazole Schiff base ligands and their metal complexes are biologically active[3] and are known for their biological application[4]. Due to biological potency, pharmacological properties and synthetic flexibility of thiazole Schiff bases. One of the drug in cytotoxicity of anticancer[5]. The aim of present investigation is to synthesize various transition metal complexes of Schiff base derived from 2-hydroxy-5-methyl-3-nitro acetophenone and 2-amino-4-phenylthiazole.

EXPERIMENTAL

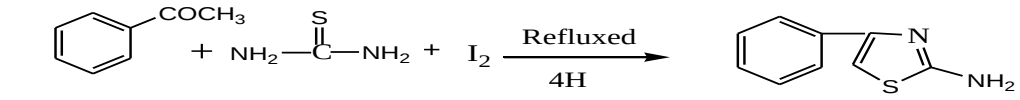
All the chemicals were of A.R. grade and used as received. 2-hydroxy-5-methyl-3-nitro acetophenone (HMNA) and 2-amino-4-phenylthiazole was prepared by known methods[6-9]. The solvents were purified by standard methods[10].

Synthesis of 2-amino-4-phenylthiazole;

The synthesis of 2-amino-4-phenylthiazole prepared by known method[7-9]. The product was filtered and crystallized from 70% ethanol, after several minutes the golden coloured product of 2-amino-4-phenylthiazole was separated out.

Yield: (75%); m.p.: 148-150^{0}C

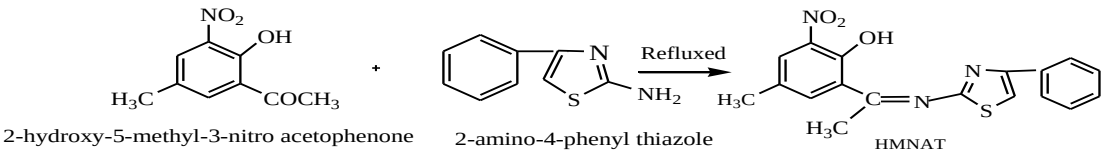
IR Spectrum: υ, cm^{-1} 3420, 3240(NH_2, Two bands); 3170(CH of C_3HNS); 3100 (CH of C_6H_5); 420, 1500, 1575 (C=C of C_6H_5); 1460(C=N)



Acetophenone — 2-amino-4-phenylthiazole

Synthesis of 2-hydroxy-5-methyl-3-nitroacetophenone 4-phenyl-2 imino thiazole [HMNAT]:

A solution of 4-phenyl-2 imino thiazole (0.02M) in 25ml of ethanol was added to an ethanolic solution(25ml) of 2-hydroxy-5-methyl-3-nitro acetophenone (0.02M) and the reaction mixture was refluxed on a water bath for 4h. After cooling a pale yellow coloured crystalline solid was separated out. It was filtered and washed with ethanol, crystallized from DMF and dried under reduced pressure at ambient temperature. The purity of ligand was checked by elemental analysis and m.p. It was also characterized by IR and ^{1}H NMR spectral studies. Yield:7o%; m.p. 310^{0}C



2-hydroxy-5-methyl-3-nitro acetophenone — 2-amino-4-phenyl thiazole — HMNAT

Table1. Analytical data of the Ligands.

Ligand	Molecular Formula	Formula Weight	Color and nature	Elemental Analysis		
				C% found (Cal.)	H% Found (Cal.)	S% Found (Cal.)
HMNAT	$C_{18}H_{15}N_3O_3S$	353.1	Yellow Crystalline	54.42 (61.17)	04.24 (03.39)	08.34 (09.06)

Preparation of complexes:

All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HMNAT (0.02M) in 25ml of ethanol a suspension of respective metal salts was added drop wise with constant stirring. The reaction mixture was refluxed on a water bath for 3-5 h. The precipitated complexes were filtered, washed with ethanol followed by ether and dried over fused calcium chloride. Yield : 55-60%

The complexes are soluble in DMSO and DMF but insoluble in water and common organic solvents. The metal chloride content of complexes were analyzed by standard methods[11-12]. The ^{1}H NMR spectra of ligand was recorded and obtained from RSIC Chandigarh. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000cm^{-1}, Carbon, Hydrogen and Nitrogen analysis were carried out at RSIC, Punjab University, Chandigarh. The molar conductance of the complexes at 10^{-3} M dilution in DMF were determined using equiptronic digital conductivity meter EQ-660 with a cell constant 1.00 cm^{-1} at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using $[HgCo(SCN)_4]$ as the calibrant. The thermogravimetric analysis were performed on laboratory set up apparatus in air atmosphere at 10^0 C min^{-1} heating rate. The molecular weights of the complexes were determined by Rast method.

Table 2. Analytical data and molar conductance of the compounds.

Ligand	Formula weight g mole^{-1}	Colour	Elemental Analysis Found (Calcd.)			μ_{eff} B.M	Λ_M (Ω^{-1} cm^2 mol^{-1})
			M%	C%	H%		
$[CoL_2(H_2O)_2]\ H_2O$	817.1	Brown	6.18 (7.20)	45.82 (52.86)	4.35 (4.40)	4.4	7.4
$[NiL_2(H_2O)_2]\ H_2O$	816.9	Green	6.31 (7.08)	46.54 (52.88)	4.17 (4.16)	3.2	8.2
$[CuL_2(H_2O)_2]\ H_2O$	821.7	Brown	6.94 (7.65)	46.12 (52.57)	4.28 (4.13)	1.6	8.2
$[ZnL_2\ (OH)_2]\ 2H_2O$	873.6	Yellow	6.41 (7.31)	44.14 (49.45)	3.12 (3.89)	Dia	12.4

RESULT AND DISSCUTION

The Schiff base HMNAT and its complexes have been characterized on the basis of ^{1}H NMR, IR spectral data, elemental analysis, molar conductance, magnetic succeptibility measurements and thermogravimetric analysis data . All these values and analytical data is consistent with proposed molecular formula of ligand . All the compounds are coloured solid and stable in air. They are insoluble in water but soluble in coordinating solvents like DMF and DMSO. The molar conductance values in DMF(10^{-3} M) solution at room temperature (Table2) shows all the complexes are non electrolytes.

The ^{1}H NMR spectra of ligand HMNAT shows signals at δ 12.24,(1H, s phenolic OH), δ 7.60, 7.74, 7.63 and 7.72 (4H, m, phenyl) δ 6.87, 6.88, and 6.72(3H, s Phenyl), 6.78 (1H s thiophene), and 2.66(3H, s, methyl)[11-15].

IR spectra of ligand and metal complexes shows ν(C=N) peaks at 1626 cm^{-1} and absence of C=O peak at around 1700 – 1740 cm^{-1} indicates the Schiff base formation[16-19].

Table 3. IR spectra of ligand and metal complexes

Compound	ν(O–H) hydrogen bonded	ν(C=N) imine	ν(C–O) phenolic	ν(M–O)	ν(M–N)	ν(C–S)
HMNAT (LH)	3085	1626	1520	--	--	1128
$[CoL_2(H_2O)_2]\ H_2O$	--	1606	1504	472	431	1092
$[NiL_2(H_2O)_2]\ H_2O$	--	1583	1466	465	422	1094
$[CuL_2(H_2O)_2]\ H_2O$	--	1615	1504	502	416	1114
$[ZnL_2(OH)_2]\ 2H_2O$	--	1612	1495	443	413	1105

Thermogravimetric studies:
Thermogravimetric study indicates all the complexes are stable up to 60-70^{0}C. All the complexes shows half decomposition temperature(Table 4). The Thermal activation energy was calculated by Freeman-Carroll,[20] Horowitz-metzger[21] and Broido[22] method.

Table 4. Thermal decomposition data of HMNAT and its complexes.

Compounds	Half Decompo-sition Temp. (^{o}C)	Activation Energy (kJ mole^{-1})			Frequency Factor Z (sec^{-1})	Entropy Change -ΔS (J mol^{-1} K^{-1})	Free Energy Change ΔF (kJ mol^{-1})
		B*	H-M**	F-C***			
HMNAT (LH)	266.51	3.25	4.42	4.52	87.10	210.65	115.65
$[CoL_2(H_2O)_2]\ H_2O$	402.21	5.22	8.62	6.84	138.77	210.52	148.53
$[NiL_2(H_2O)_2]\ H_2O$	388.11	6.72	8.32	6.41	134.37	210.66	146.36
$[CuL_2(H_2O)_2]\ H_2O$	424.31	6.53	8.44	7.43	150.58	210.39	155.15
$[ZnL_2(OH)_2]\ 2H_2O$	712.41	11.13	18.51	11.21	222.22	209.56	217.68

CONCLUSIONS

In conclusion, we have synthesized new ligand 2-hydroxy-5-methyl-3-nitroacetophenone 4-phenyl-2 imino thiazole and their metal complexes with concluded water loss in metal complexes and ligand. This paper also concluded half decomposition temperature and parameter of activation energy.

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REFERENCES

[1] K. Singh, M.S. Barwa and P. Tyagi, Eur. J. Med. Chem.,. 42, 394, 2007.
[2] P.G. Cozzi, Chem. Soc. Rev., 33, 410, 2004.
[3] S. Raziya, S. Mohan and S. Rao, Indian J. Chem., 46B, 884, 2007.
[4] S. Kumar, D. Dhar and P. Saxena, J. Sci.and Indu.Research, 68, 181, 2009.
[5] T. Reji, S. Devi, K.Thomas, K. Sreejalekshmi, S. Manju, M. Francis, S. Philip, A. Bharathan, and K. Rajasekharan, Indian j. Chem., 47B, 1145, 2008.
[6] A. Aswar, P. Bahad, A. Pardhi and N. Bhave, J. Poym. Mater. 5, 232 1988.
[7] S. Pattan, M.Ali, J. Pattan, S. Purohit, V. Reddy and B. Nataraj, Indian J. Chem., 45B, 1929, 2006.
[8] D. Khrustalev, A. Suleimenova and S. Fazylov, Russian J. App. chem., 81(5), 900, 2008.
[9] H. Maradiya, and V. Patel, J. Fibers and poly., 3(1), 43, 2002.
[10] B. Furniss, A. Hannaford, P. Smith & A. Tatchell, Vogel's practical organic chemistry 5 thEd. (Logman Scientific Technical, John Wiley and Sons), (1989).

[11] S. Sadigova, A. Magerramov and M. Allakhverdiev, Russian J. Org. chem., 81(5), 900, 2008.
[12]Vogel AI, "A Text book of quantitative inorganic chemistry"3thEd., (ELBS,London,1961).
[13] E. Campbell and S.Nguyen, J. Tetrahedron, 42, 1221, 2001.
[14] P. Pietikainen and A. Haikarainen J. Mole. Catalysis., 180, 59, 2002.
[15] M. Kidwai, P. Poddar and K. Singhal, Indian J. Chem., 48B, 59, 2009.
[16] S. Sonwane, and S. Srivastava, Indian J. Chem., 47B, 633, 2008.
[17] K. Patel and A. Mehata, E. J. Chem., 3(13), 267, 2006.
[18] R. Maurya, D. Antony, S. Gopinathan, V. Puranic, S.Tavale and C. Gopinathan, Bull. Chem. Soc. Jpn., 68, 2847, 1995.
[19] D. Boghaei and S. Mohebi, J. Tetrahedron, 58, 5357, 2002.
[20] K. Mallikarjun, E. J. Chem., 1(2), 105, 2004.
[21] H. Horowitz and G. Metzger, Anal. Chem., 35, 1464, 1963.
[22] A. Broido, J. Polym. Sci. Part, A2, 1761, 1964.

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