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"SYNTHESIS AND SPECTRAL STUDIES OF Co(II) AND Ni(II) COMPLEXES WITH SCHIFF BASE LIGAND 1,6-DIMERCAPTO-1,6 DIAMINO-2,4,5-TRIAZA-3-PHENYL-3-HEXENE"

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ABSTRACT

Complexes of 1,6 Dimercapto 1,6 Diamino 2,4,5 Triaza 3-Phenyl 3-hexene (MAAPHE) with bivalent metal ion of composition $[ML_2]X_2$ M= Co(II) and Ni(II), X=Cl^-, Br^-, NO_3^- have been synthesized and characterized using physico-chemical and spectroscopic data. The ligands were found to be neutral tridentate chelating ligand for the metal ions and the complexes are found to be octahedral in geometry.

Keywords : 1,6-dimercapto-1,6-diamino-,2,4,5-triaza-3-phenyl-3-hexene; Co(II) and Ni(II) complexes, Tridentate, Octahedral.

INTRODUCTION

Schiff bases and related complex compounds have gained importance because of their uses in analytical, biological, biochemical and antimicrobial system due to presence of multiheterofunctional group[1,2]. When such ligands are complexed with the metal ions they enhanced antibacterial activities. The present progress of synthesis and characterization of a series of complexes of Co(II) and Ni(II) with MAAPHE are reported.

EXPERIMENTAL

All the chemicals used were of AR grade. Solvent used were double distilled. The Schiff base ligand 1,6-dimercapto-1,6-diamino-,2,4,5-triaza-3-phenyl-3-hexene (MAAPHE) was derived by refluxing equimolar concentration of thiosemicarbazide and N-Benzoylthiourea in ethanolic medium for 5 hours. The resulting products were cooled a raw silky crystals were separated. The crystal were filtered, washed successively with DMF, cold ethanol and dried in a vaccum desicator over fused $CaCl_2$ and analyzed (m.p. = 232 ± 2^0C, yield 70%) as $C_9H_{11}N_5S_2$ and gave satisfactory C,H,N and S analyses.

Table 1

Elements	Found %	Calculated %
C	42.62	42.68
H	4.35	4.34
N	26.75	26.66
S	25.31	25.29

Preparation of the complexes

The complexes of Co(II), and Ni(II) have been formed by refluxing together Schiff base ligand MAAPHE with metal salts in molar ratio 2:1 of the type $[M(MAAPHE)_2]X_2$ where M=Co(II), Ni(II) and X=Cl^-, Br^-, NO_3^- etc. The solid coloured complexes are separated on cooling, were filtered, washed with ethanol and dried.

All the experimental details gave satisfactory C,H,N,S and metal analyses.

The IR spectra were recorded on Beckmann IR-20 spectrophotometer using KBr pellets. The molar conductivity were carried out on conductivity bridge using 10^{-3}M DMF solution, magnetic moment were determined by Gouy method using $Hg[Co(CNS)_4]$ as a calibrant.

The analytical data, colour, magnetic susceptibility electronic spectra and conductivity are recorded in Table 2.

Table 2

Compound / colour	% of Analysis found (cal.)					μ eff	Molar cond.	λ max
	M	C	N	H	S	B.M.	$\Omega^{-1}cm^2mol^{-1}$	(electronic)
MAAPHE (silky) (Silky)		42.62 (42.68)	26.75 (26.66)	4.35 (4.34)	25.31 (25.29)			
$[Co(MAAPHE)_2]Cl_2$ (green)	9.22 (9.27)	34.02 (33.96)	21.98 (22.01)	3.48 (3.46)	20.32 (20.12)	5.21	155	16750, 26000
$[Co(MAAPHE)_2]Br_2$ (yellowish green)	8.05 (8.13)	29.71 (29.79)	19.34 (19.31)	3.08 (3.03)	17.60 (17.65)	5.28	159	17000, 25500
$[Co(MAAPHE)_2](No_3)_2$ (brown)	8.47 (8.56)	31.39 (31.34)	20.37 (20.32)	3.10 (3.19)	18.63 (18.58)	5.17	164	17200, 26300
$[Ni(MAAPHE)_2]Cl_2$ (green)	9.16 (9.23)	33.89 (33.97)	22.11 (22.02)	3.48 (3.46)	20.09 (20.14)	3.01	148	13200, 18950, 22450
$[Ni(MAAPHE)_2]Br_2$ (deep green)	8.13 (8.09)	29.76 (29.80)	19.25 (19.31)	3.10 (3.03)	17.59 (17.66)	2.95	144	13900, 18750, 26100
$[Ni(MAAPHE)_2](No_3)_2$ (yellowish green)	8.60 (8.52)	31.31 (31.36)	20.29 (20.33)	3.21 (3.19)	18.49 (18.58)	3.09	148	14200, 18750, 25700

RESULTS AND DISCUSSION

The IR spectra of the ligands MAAPHE as well as the metal complexes have been measured in the region 4000-200 cm^{-1} shown in Table 3

The spectra of the ligand exhibits a group of strong and broad bands in the range 3400-3100 cm^{-1} of combined mode of n_{N-H}, n_{S-H} and n_{NH} suggesting ligands to exist in Thioketo/Thiol form in the solid state. These bands are not affected in the spectra of the complexes indicating the non participation of amino group. The ligand molecules contains NCSH and HNCS units, suggesting thiomide bands in IR spectra[3]. The bands at 1695 cm^{-1} and 950 cm^{-1} are assigned to $n_{C=N}$ and n_{N-N} respectively[4].

In IR spectra of ligands a band observed around 1680 cm – 1695 cm^{-1} with decreased sharpness and intensity indicating the participation of azomethine nitrogen in complexation[5-8]. The n_{N-N} band in the complexes appears at 900-925 cm^{-1} showing red

Table 3

IR spectra of Co(II) & Ni(II) complexes

Compound	$n_{N-H} + n_{N-H} + n_{S-H}$	$n_{C=N}$	$n_{C=S}$	n_{N-N}	n_{M-S}	n_{M-N}
MAAPHE	3400-3100 cm^{-1}	1695 m,b	780 m,b	950 m		
$[Co(MAAPHE)_2]CL_2$	3400 – 3100 cm^{-1}	1685 m,b	710 m,b	915 m	410 m	455 m
$[Co(MAAPHE)_2]Br_2$	“	1680 m,b	715 m,b	910 m	400 m	450 m
$[Co(MAAPHE)_2](NO_3)_2$	“	1690 m,b	710 m,b	915 m	410 m	450 m
$[Ni(MAAPHE)_2]CL_2$	“	1690 m,b	715 m,b	900 m	415 m	450 m
$[Ni(MAAPHE)_2]Br_2$	“	1685 m,b	720 m,b	910 m	405 m	455 m
$[Ni(MAAPHE)_2](NO_3)_2$	“	1680 m,b	715 m,b	930 m	410 m	450 m

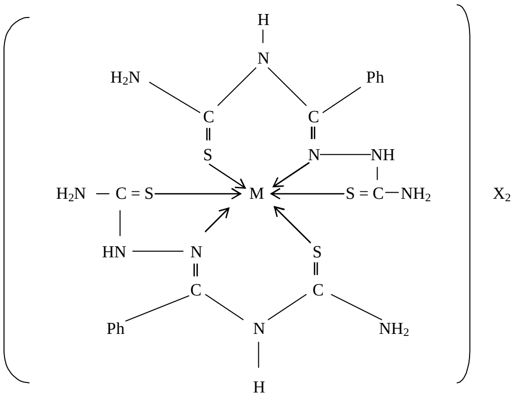
shift as compared to the ligand. The $n_{C=S}$ band at 780 cm^{-1} in the ligand also experiences a downward shift[9] in the metal complexes and appears at 710 cm^{-1}. It suggests that participation in co-ordination of the thione sulphur metal ions. In the far IR region new additional bands in the region 450-455 cm^{-1} and 400-420 cm^{-1} may be assigned to n_{M-N} and n_{M-S} respectively[10-12].

The electronic spectra of Co(II) complexes have been reported having ligand field transitions appears in the visible region being intense $^{4}T_{1g}$(P) ß $^{4}T_{1g}$ (F) in the region 16600 cm^{-1} – 17500 cm^{-1} and the change transfer band spreading over, the region 25500-28000 cm^{-1} which indicates the octahedral geometry, which are further supported[13-15] by high meff value of $[Co(MAAPHE)_2]X_2$ type compound possesses 5.11 to 5.30 B.M.

The electronic spectra of Ni(II) complexes consist of three bands in the region 13000-14000 cm^{-1} [$^{3}T_{2g}(F) \leftarrow {}^{3}A_{2g}(F)$], the next one in the vicinity of 20000 cm^{-1} [$^{3}T_{2g}(F) \leftarrow {}^{3}A_{2g}(F)$] and the strong intense band near to 26000 cm^{-1} ($^{3}T_{1g}$ (P) $\leftarrow$ $^{3}A_{2g}$ (F). The magnetic moment value of $[Ni(MAAPHE)_2]X_2$ is in the range of 2.9 – 3.15 B.M. suggest octahedral geometry[16].

Conductivity of the complexes of the type $[M(MAAPHE)_2]X_2$ were measured in the solvent dimethyl formamide at the concentration 10^{-3} M and all the complexes were found to be electrolyte[17] in nature of the 1:2 type and conductivity values are in the range 140-170 ohm^{-1} cm^{2} mol^{-1}.

On the basis of above discussion on the spectral results vide supra the complexes may be assigned octahedral geometry and MAAPHE ligands behaves as tridentate NSS donor.



M=Co(II), Ni(II), Ph=Phenyl, X=Cl^{-}, Br^{-} & NO_3^{-}

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