

Mixed Ligand Complexes of N-6-methyl Benzothiazol-2-yl-salicylaldimine and 2-methyl Benzimidazole with Cu(II), Ni(II), Co(II), Mn(II), VO(II), Zn(II), Cd(II) and Hg(II)

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Abstract. Mixed-ligand complexes of the type $MS_2(MeBI)_2$ (where $M = Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II), Hg(II)$, SH = N-6-methyl benzothiazol-2-yl-salicylaldehyde and $MeBI = 2$ -methyl benzimidazole) and $VOS_2.MeBI$ have been synthesised and characterised on the basis of analysis, molar conductances, magnetic moments, electronic and i.r. spectral data. All the complexes, were found to be non-electrolyte and possessed octahedral geometry.

1. Introduction

Several research papers¹⁻⁴ have been published on transition metal complexes of schiff base derived from salicylaldehyde. Transition metal complexes with substituted salicylaldehyde ligands offer a diversity of structure and properties involving a number of stereochemistries and a wide range of bonding interaction^{5,6}. The present paper describes the results of our investigations on mixed schiff base complexes.

2. Experimental

All the chemicals used were of AnalaR grade. 6-Methyl-2-amino benzothiazole was prepared by the method of Hugershoff⁷.

2-N-6-Methyl benzothiazolyl salicylaldehyde (SH) was prepared according to the method of Chaurasia and Shukla⁸ m. pt. 110°.

Preparation of $MS_2(MeBI)_2$ [$M = Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II)$ and $Hg(II)$]

The ethanolic solutions of metal salts, SH and 2-methyl benzimidazole ($MeBI$) were mixed in 1:2:2 molar ratio and the reaction mixtures were refluxed for an hour.

The excess of alcohol was distilled off. The final products were washed with distilled water, then with 10 per cent alcohol and dried in vacuo over anhydrous calcium chloride.

$VOS_2 \cdot MeBI$ was prepared by mixing the ethanolic solution of $VOSO_4 \cdot 2H_2O$, SH and $MeBI$ in 1:2:1 molar ratio. The reaction mixture was heated for an hour at 70° . The complex was recovered as stated above.

Molar conductance was measured on a WTW Conductivity meter in acetone. The magnetic susceptibility of the complexes was determined by the Faraday method, using $Co [Hg(SCN)_4]$ as calibrant. The diamagnetic corrections were applied by the method of Figgis and Lewis⁹. Analytical data, molar conductances and magnetic moments of the complexes are given in Table 1.

Table 1. Analytical data, molar conductances and magnetic moments of the complexes.

Complex	M. Pt (°C)	Metal (per cent)		Nitrogen (per cent)		Molar con- ductance (cm ² mho ² /mole)	μ eff (B.M.)
		Found	Calcd.	Found	Calcd.		
$CuS_2 \cdot (MeBI)_2$	102	7.21	7.38	12.78	12.99	0.04	1.79
$NiS_2 \cdot (MeBI)_2$	92	6.62	6.85	13.47	13.07	0.05	3.33
$CoS_2 \cdot (MeBI)_2$	59	6.49	6.88	13.38	13.17	0.02	4.85
$MnS_2 \cdot (MeBI)_2$	49	6.28	6.44	13.26	13.13	0.06	6.10
$ZnS_2 \cdot (MeBI)_2$	76	7.38	7.57	12.42	12.97	0.00	dia.
$CdS_2 \cdot (MeBI)_3$	56	12.12	12.35	12.12	12.30	0.02	
$HgS_2 \cdot (MeBI)_2$	55	20.39	20.09	11.42	11.26	0.02	"
$VOS_2 \cdot MeBI$	77	6.79	6.95	11.62	11.46	0.01	1.80

The electronic spectra of the complexes were recorded on Carry-14 and VSU-2Ph spectrophotometers. The values of the ligand-field parameters are given in Table 2.

The infrared spectra of the complexes and ligands were recorded on Perkin-Elmer spectrophotometer (model-720) in 4000–650 cm^{-1} range in KBr . The important i.r. bands and their assignments are given in Table 3.

Table 2. Ligand field parameters of the complexes.

Complex	$10Dq$ (cm^{-1})	B' (cm^{-1})	β	β^0 (%)	ν_2/ν_1 (cm^{-1})	λ' (cm^{-1})	$\zeta 3d$ (cm^{-1})	LFSE (kJ/mole)
$CuS_2 \cdot (MeBI)_2$	12820	—	—	—	—	—222.32	222.32	91.96
$NiS_2 \cdot (MeBI)_2$	8333	1023.2	0.969	3.23	1.76	—368.06	736.2	115.95
$CoS_2 \cdot (MeBI)_2$	8124	757.03	0.78	22.12	2.02	—	—	77.7
$VOS_2 \cdot MeBI$	16129	—	—	—	—	—326.31	326.31	77.13

3. Results and Discussion

The values of the molar conductance are very low showing the non-electrolytic nature of the complexes¹⁰.

Table 3. Important infrared bands (cm^{-1}) and their assignments of metal complexes of N-6-methyl benzothiazol -2-yl-salicylaldimine and 2-methylbenzimidazole

Complex	(C = N)	(C - O)	MeBI
SH	1625s	1280s	3300m, 1390s
$\text{CuS}_2(\text{MeBI})_2$	1650s	1300m	3250w, 1350s
$\text{NiS}_2(\text{MeBI})_2$	1630s	1300m	3200w, 1360s
$\text{CoS}_2(\text{MeBI})_2$	1650w	1340w	3200w, 1370s
$\text{MnS}_2(\text{MeBI})_2$	1630w	1325w	3250w, 1375s
$\text{ZnS}_2(\text{MeBI})_2$	1640m	1310m	3415w, 1400w
$\text{CdS}_2(\text{MeBI})_2$	1630sh	1310m	3425w, 1400w
$\text{HgS}_2(\text{MeBI})_2$	1630sh	1310m	3430w, 1380s
$\text{VOS}_2 \cdot \text{MeBI}$	1630s	1305m	3350b, 1375s

The magnetic moment data indicate octahedral geometry for all the complexes⁹. The magnetic moment of $\text{MnS}_2(\text{MeBI})_2$ is close to values expected for spin-free manganese(II) complexes with five unpaired electrons.

The vanadyl complex, $\text{VOS}_2 \cdot \text{MeBI}$ has normal magnetic moment (1.72–1.94 B.M.) expected for an unpaired electron species.

The Zn(II), Cd(II) and Hg(II) complexes are diamagnetic and suggest octahedral structure involving the use of Sp^3d^2 type of hybridization.

The electronic absorption spectrum of SH exhibits four absorption bands at 45454, 35088, 25641 and 21739 cm^{-1} . The first two bands are assigned to $\pi - \pi^*$ transitions¹¹. The latter two sharp bands are attributable to $n - \pi^*$ transitions arising from $-\text{OH}$ and $-\text{C} = \text{N}$ in an extensively conjugated π -electron system.

$\text{CuS}_2(\text{MeBI})_2$ yields one broad band at 12820 cm^{-1} due to ${}^2E_g \rightarrow {}^2T_{2g}$ transition which indicates octahedral geometry around the complex¹². The other intra-ligand bands are 44444, 35714, 23616, 20000, 17857 and 13514 cm^{-1} . The bands observed in the spectrum of Cu(II) complex is considerably blue shifted compared to the first band maxima of the corresponding Ni(II) complex owing to John-Teller distortion of 2E_g state. The ratio $\nu_{\text{Cu}}/\nu_{\text{Ni}}$ comes out to 1.42 indicating considerable distortion¹³ in the octahedral geometry of the complex.

In $\text{NiS}_2(\text{MeBI})_2$ complex, three bands at 8333, 14706 and 25641 cm^{-1} respectively, corresponding to transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1), ${}^3T_{1g}$ (F) (ν_2), ${}^3T_{1g}$ (P) (ν_3), have been observed. The above bands are characteristics of octahedral Ni(II) complex⁵. This observation is further supported by the ratio ν_2/ν_1 transition which lies within the range (1.8 and 1.6) for octahedral Ni(II) complexes¹⁴. The other intra-ligand bands are 37736, 33333 and 26316 cm^{-1} .

For octahedral Ni(II) complexes, calculations¹⁵, which include mixing of the ${}^3A_{2g}$ ground state with the ${}^3T_{2g}$ excited state, give the following equation for the g value (Lunde's g factor): $g = 2 - 8 \lambda'/10Dq$ (where λ' = spin-orbit coupling constant). In hexa quo nickel(II) it is found that $g = 2.25$. Using the above equation the $\text{NiS}_2(\text{MeBI})_2$ complex has $g = 2.35$. The $10Dq$ and λ' values of the complex are 8333 and -368 cm^{-1} respectively. In a molecular orbital description¹⁶, the extent of mixing of the metal and ligand orbitals, illustrate the effect of spin-orbit coupling and Dq on the magnitude of g value.

The bands, observed at 8000 and 19231 cm^{-1} in the spectrum of the $\text{CoS}_2(\text{MeBI})_2$ complex, are typical of $\text{Co}(\text{II})$ complex in the octahedral¹⁷ environment. The first band may be identified as ${}^4T_{1g} \rightarrow {}^4T_{2g}(\text{F})$ transition and the second band as ${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P})$. The transition energy ratio ν_2/ν_1 in the range 1.95–2.06 is in accordance with the literature data for octahedral $\text{Co}(\text{II})$ complexes¹⁸.

The spectrum of $\text{VOS}_2 \cdot \text{MeBI}$ complex yields only two bands at 12821 and 16129 cm^{-1} , assigned to $dxy \rightarrow dyz$, dxz and $dxy \rightarrow dx^2 - y^2$ transitions respectively, indicating distorted octahedral geometry of the complex¹⁹. The other bands observed are 43478, 37037 and 26316 cm^{-1} .

In $\text{MnS}_2(\text{MeBI})_2$, one intense and sharp band at 25641 cm^{-1} and other relatively less intense and broad band at 14706 cm^{-1} are observed, assignable to a charge transfer²⁰ and $d - d$ transition²¹ respectively.

Using the above assignments, the various spectral parameters viz., 10Dq, Racah parameter (B'), nephelauxetic ratio (β), percentage lowering of the energy of the 3p state in the complex compared to the energy of 3p in the free gaseous ion (β°), ligand field stabilization energy (LFSE), spin-orbit coupling constant (λ') and spin orbit coupling constant per electron ($\zeta 3d$) have been calculated by the method outlined by Lever²².

The broad band in the ligand (SH) at 3450 cm^{-1} , is absent in the complexes, indicating that the $-\text{OH}$ group is taking part in complexation. The $\text{C} = \text{N}$ band at 1625 cm^{-1} in the free ligand, is shifted to (5–25 cm^{-1}) higher frequency range in all the complexes, provides evidence for $\text{C} = \text{N}$ coordination to the metal ions²³. The shift in the $\text{C} - \text{O}$ stretching frequency, observed in the free ligand at 1280 cm^{-1} to higher frequencies (1300 – 1340 cm^{-1}) in the complexes, is indicative of the coordination through phenolic $-\text{OH}$ ²⁴. The $\nu(\text{C} - \text{S} - \text{C})$ and $\nu(\text{C} = \text{N})$ (cyclic) at 830 and 1550 cm^{-1} in the ligand remain unchanged in the spectra of the complexes showing the absence of coordination through sulphur and $\text{C} = \text{N}$ groups. It is evident from the discussion that the phenolic oxygen and exocyclic nitrogen atoms are bonded to the metal ions in the complexes.

The complexes show additional ($\text{N} = \text{H}$) bending and stretching frequencies at near about 1400 and 3300 cm^{-1} respectively indicating that the 2-methyl benzimidazole is coordinated through the tertiary nitrogen atom, as confirmed by X-ray structural studies earlier²⁵.

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