

STUDIES OF SOME BI-VALENT TRANSITION METAL COMPLEXES OF SOME SCHIFF BASES

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ABSTRACT : In this paper the some bi-valent transition metal complexes such as Mn(II), Co(II), Ni(II) and Cu(II) with some Schiff base derived from 2-furyl glyoxal-4'-iminobenzene sulphonamide, 2-furyl-N-acetyl-4'-iminobenzene sulphonamide and 2-furyl glyoxal-N-imino N-phenyl thiocarbamide have been synthesized. These complexes have been characterized on the basis of their element analysis, magnetic susceptibility measurements, electronic and IR spectral data.

Keywords: Bi-valent Transition metals, Schiff Bases, Micro analysis instruments, Spectrophotometer.

INTRODUCTION :

In this paper have recently been synthesized a number of bi-valent transition metal complexes of some Schiff base ligands having nitrogen, oxygen and sulphur as a donor Set¹. These complexes are of great important due to their unique pharmacological and therapeutic application^{2,3}. In the present paper the synthesis and characterization of Some bi-valent transition metal complexes such as Mn(II), Co(II), Ni(II) and Cu(II) complexes of some Schiff bases derived from 2-furyl glyoxal and 4'-iminobenzene sulphonamide, N-acetyl-4, iminobenzene sulphonamide and N-imino-N-phenyl thiocarbamide are reported.

MATERIAL AND METHODS

The preparation of Schiff bases of ethanolic solution of 2-furyl glyoxal was added to an ethanolic solution of 4'-iminobenzene sulphonamide, or N-acetyl-4'-iminobenzene sulphonamide or-N-imino-N-phenyl thiocarbamide, in an equimolar ratio. The solution mixture was refluxed on water bath for about four hours. The excess solvent was removed by distillation. The solution was kept for a day when a coloured precipitate of Schiff base was obtained which was filtered, washed with alcohol and dried.

The Preparation of complexes ethanolic solution of metal chloride was added to ligand solution in ethanol in 1:1 molar ratio. The reaction mixture was refluxed for about four hours. The contents were cooled and the volume of the solvent was kept overnight at room temperature. A coloured product separated out which was filtered, washed and dried.

The micro analysis of carbon and hydrogen Thomas and C.H. analyser-35" was used. The standard method was used for the determination of percentage of sulphur in complexes whereas nitrogen was estimated by Kjeldhal's method. The estimation of halogen was carried out by Vohlard's method. The magnetic susceptibility measurements of the complexes were carried out at room temperature on Gouy's balance. The electronic spectra of complexes in solution state were run on spectronic-20D spectrophotometer in the range 955-320 nm at room temperature. The I.R. spectra of the ligand and their metal chelates were recorded in KBr and CsI pallets on Perkin Elmer 577 spectrophotometer in the region 4000-200cm⁻¹.

RESULTS AND DISCUSION

Analytical and physical data are given in Table-1. All the complexes are insoluble in common organic solvents such as methanol, ethanol and chloroform while soluble in DMF, dioxane and acetone. The analytical data indicates 1:2 metal ligand stoichiometries for all complexes.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF SOME BI-VALENT TRANSITION METAL COMPLEXES

Compound	Colour	M.P. Analysis found/ Calculated					μ_{eff}			(BM)
		$^{\circ}\text{C}$	C	H	N	S	M	CI		
(C ₁₂ H ₁₀ N ₂ SO ₄)	Brown	126	44.91 (44.99)	3.20 (3.14)	20.82 (20.87)	9.99 (10.01)	-	-	-	-
(C ₁₄ H ₁₂ N ₂ SO ₅)	Orange Red	176	57.38 (57.13)	3.72 (3.14)	8.69 (8.75)	10.81 (10.89)	-	-	-	-
(C ₁₃ H ₁₀ N ₂ SO ₂)	Violet Black	180	60.39 (60.47)	3.82 (3.88)	10.77 (10.85)	12.15 (12.21)	-	-	-	-
[Mn(C ₁₂ H ₁₀ N ₂ SO ₄) ₂ Cl ₂]	Dark Brown	110	42.40 (42.45)	2.58 (2.65)	7.98 (8.02)	9.62 (9.67)	7.84 (7.89)	10.41 (10.51)	5.70	5.70
[Mn(C ₁₄ H ₁₂ N ₂ SO ₅) ₂ Cl ₂]	Almond	182	43.09 (43.15)	3.44 (3.52)	6.99 (7.01)	8.10 (8.11)	7.01 (7.05)	8.91 (8.98)	5.89	5.89
[Mn(C ₁₃ H ₁₀ N ₂ SO ₂) ₂ Cl ₂]	Grey Black	168	47.94 (48.05)	3.45 (3.51)	8.09 (8.15)	9.05 (9.11)	8.06 (8.15)	10.65 (10.79)	5.79	5.79
[CO(C ₁₂ H ₁₀ N ₂ SO ₄) ₂ Cl ₂]	Brown	250	41.47 (41.52)	2.85 (2.62)	8.01 (7.97)	9.18 (9.10)	8.27 (8.21)	9.91 (9.99)	4.53	4.53
[CO(C ₁₄ H ₁₂ N ₂ SO ₅) ₂ Cl ₂]	Light Brown	190	43.16 (43.21)	2.09 (2.14)	6.97 (7.02)	8.19 (8.13)	7.52 (7.45)	9.05 (8.99)	4.71	4.71
[CO(C ₁₃ H ₁₀ N ₂ SO ₅) ₂ Cl ₂]	Black	300	48.48 (48.51)	2.98 (2.97)	8.11 (8.18)	9.59 (9.65)	9.10 (9.02)	10.81 (10.72)	4.65	4.65
[Ni(C ₁₂ H ₁₀ N ₂ SO ₄) ₂ Cl ₂]	Brown	250	41.95 (41.82)	2.45 (2.51)	8.12 (8.06)	9.20 (9.11)	8.32 (8.25)	10.05 (9.98)	3.75	3.75
[Ni(C ₁₄ H ₁₂ N ₂ SO ₅) ₂ Cl ₂]	Brownish Yellow	170	43.35 (43.21)	3.10 (3.02)	7.20 (7.11)	8.15 (8.08)	7.51 (7.43)	8.92 (8.87)	3.20	3.20
[Ni(C ₁₃ H ₁₀ N ₂ SO ₂) ₂ Cl ₂]	Black Brown	Above 300	48.21 (48.12)	3.12 (3.32)	8.51 (8.42)	9.71 (9.63)	9.00 (8.87)	10.75 (10.69)	3.72	3.72
[Cu(C ₁₂ H ₁₀ N ₂ SO ₄) ₂ Cl ₂]	Greenish Brown	185	41.65 (41.52)	2.75 (2.68)	8.12 (8.08)	9.21 (9.12)	9.05 (9.11)	10.35 (9.98)	1.90	1.90
[Cu(C ₁₄ H ₁₂ N ₂ SO ₅) ₂ Cl ₂]	Black	174	43.22 (43.12)	3.39 (3.42)	7.38 (7.44)	1.25 (8.12)	8.15 (8.09)	9.87 (9.22)	1.95	1.95
[Cu(C ₁₃ H ₁₀ N ₂ SO ₂) ₂ Cl ₂]	Brown	196	47.81 (47.78)	3.09 (3.15)	8.50 (8.42)	8.81 (8.72)	9.76 (9.72)	10.82 (10.78)	1.85	1.85

The I.R. spectra of the ligand show two strong bands in the region 1600-1690cm⁻¹ and 1620-1650cm⁻¹ due to the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{H})$ groups respectively. These bands are shifted to lower frequencies in the spectra of their metal complexes indicating the involvement of $\text{C}=\text{O}^4$ and $\text{C}=\text{N}^5$ group in complication. The coordination through carbonyl oxygen of $\text{C}=\text{O}$ and nitrogen of azomethine group in all the complexes has been further confirmed by the appearance of $\nu\text{M}-\text{N}$, $\nu\text{M}-\text{O}$ stretching nodes⁶ at 570-540cm⁻¹ and 480-410cm⁻¹. A new band which appeared in the region 370-350cm⁻¹ in the spectra of complexes is due to $\nu\text{M}-\text{Cl}$ bond.

The electronic spectra of Mn (II) complexes exhibits four bands in the region 32786-29410cm⁻¹, 28571-21739cm⁻¹ and 19607-12821cm⁻¹ which may be assigned to the transition ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g} (4\text{D})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g (4\text{D})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g \rightarrow {}^6\text{A}_{1g} (4\text{D})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g} (4\text{D})$ respectively, The transitions ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g (4\text{D})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g \rightarrow {}^6\text{A}_{1g} (4\text{D})$ have been used to calculate the value of B and C because these transition depends

only on Band C^{7,8}. All the value of different ligand fields parameters are found to be in good agreement with those of known octahedral Mn(II) complexes. The magnetic moment values of Mn(II) complexes was found in the range 5.89-5.70 BM which shows the presence of five unpaired electrons in these complexes due to which these complexes are of high spin.

The electronic spectra of Co(II) complexes exhibit three bands at 11363-11627cm⁻¹, 15625-16129cm⁻¹ and 20833-21739cm⁻¹ which may be assigned to transitions ⁴T_{1g} → ⁴T_{2g} (F) (ν₁), ⁴T_{2g} (F) → ⁴A_{2g} (ν₂), and ⁴T_{1g} (F) → ⁴T_{1g} (P) (ν₃) respectively. The calculated value of 10Dq is in good agreement to that determined by ν₂ (observed) – ν₁ (calculated). The values of B₃₅ of these complexes are in the range 0.91-1.1 which clearly indicated the covalent character of the concerned band. The μ_{eff} value for these complexes lie in the range 4.53-4.71 BM which is slightly higher than the spin only value (2.83M) of respective metal ions, indicating the spin free octahedral environment around the metal ions⁹.

The electronic spectra of the synthesized Ni(II) complexes shows d-d transition band in the region 10416-10869cm⁻¹ and 26315-25000cm⁻¹, which may be assigned to the transitions ³A_{2g} → ³T_{2g}(ν₁), ³A_{2g} → ³T_{1g}(F), (ν₁) and ³A_{2g} → ³T_{2g}(ν₃) respectively. In all the complexes of Ni (II) ν₁/ ν₂ ratio lies in the range required for octahedral Ni (II) complexes. The calculated value of Dq and B shows the presence of strong ligand field and the covalent character of Ni complexes. The μ_{eff} values of all the Ni (II) complexes lie the range 3.13-3.75 BM, indicating that they are magnetically normal, six coordinated, spin free octahedral complexes¹⁰.

The electronic spectra of Cu(II) complexes shows three band at 15625, 15151 and 14925cm⁻¹ which indicates three transitions ²B_{1g} → ²A_{1g}, ²B_{1g} → ²B_{2g}, and ²B_{1g} → ²E_g, respectively. The ligand field stabilization energy has been calculated for these newly synthesized complexes and found within the range 106.94-111.96 which is required for octahedral Cu (II) chelates. Lower value of nephelauxetic parameters (f) (0.65-0.62) suggested that bands present in these complexes are partially covalent in nature. The μ_{eff} value these complexes laid in the ranges 1.95-1.85 BM which suggests the spin-free octahedral geometry for these complexes due to the presence of unpaired electrons.

REFERENCES

- [1] Talwar S. Usha S., Chandra S., Singh R. and Veeraswamy P., Synth React Inorg Met-Org Chem., 21(1) (1991) 131-142.
- [2] Celebi S, Ozkaley Y and Sarikahya Y, Speaktash Dery, 174 (1985)
- [3] Syamal A and Maurya M R., J. Induan Chem. Soc., 63 (1986), 1152-55.
- [4] Reddy K. L., Srihari S. and Lingaiah P., J. Indian Chem. Soc., 60 (1983), 1020.
- [5] Chanrawarti P.B. and Khanna P., J Indian. Chem. Soc., 62 (1985) 23.
- [6] Ferraro, J.R., "Low Frequency Vibrations of Inorganic and Coordination Compounds" Plenum, New York, (1971).
- [7] Preti E. And Tast G., Aust. J. Chem. Soc., 20 (1976) 543.
- [8] Orgel L.E., J. Chem. Phys., 23 (1955) 1004.
- [9] Figgis B. N. And Lewis J, Prog Inorg. Chem., 6 (1964) 197.
- [10] Eliphen R. B. And Friedberg S.A., Phys rev. 121 (1961) 1541.