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Magnetic and Electronic Spectral Studies of the Complexes formed by (2E)-2-(4-methoxybenzylidene)hydrazinecarbothioamide with Mn (II), Fe(II) and Co(II) Metal Ions

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Abstract

Metal complexes of Divalent Mn (II) and Fe (II) and Co(II) metal ions with (2E)-2-(4-methoxybenzylidene)hydrazinecarbothioamide have been prepared. These compounds were characterized by elemental analyses as well as by electronic spectral studies and magnetic measurements. Ligand synthesized was bidentate in nature and the general composition of all the complexes was found to be $[M(L_2)X_2]$ where $X = Cl^-, Br^-, I^-, NO_3^-$ & CNS^- . All the complexes synthesized were found to have a distorted octahedral geometry and were found to be high spin in nature in pseudo octahedral environment.

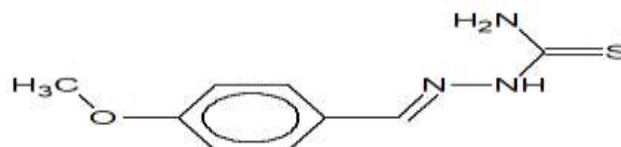
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Introduction

Coordination chemistry is considered to be the backbone for majority of present research work in chemistry or the study of complexes and specially those of transition metals. Metals of 3d series are very well known to show variable valency in their complexes due to the presence of incomplete d orbital, ease of loss of two or more electrons and availability of d orbitals for bond formation. Most of the ligand studied contain halide ions, oxygen and nitrogen as donor atoms. However Ligands with sulphur donor atoms have presented an interesting example. Electronegativity of sulphur is almost in the middle of all the electronegative atoms. Effective electronegativity is affected by the presence of other atoms or groups to donor atom. Coordinating ability of a unidentate ligand is affected by both the electronegativity as well as the total dipole moment of ligand¹.

Introduction of sulphur and nitrogen atoms in a number of organic compounds has resulted in some important outcomes towards their behaviour with transition metal ions. Among a number of well known sulphur containing ligands thiosemicarbazones (TSC) present an attractive class of metal chelating ligands because of their tendency to coordinate with the metal ion through sulphur as well as through azomethinic nitrogen atoms². They behave as multidentate ligands because of the presence of nitrogen and sulphur donor atoms and furthermore their binding properties may also be altered at the same time through the insertion of some other donor hetero atoms like oxygen.

Present studies are made by preparing complexes of (2E)-2-(4-methoxybenzylidene)hydrazinecarbothioamide or para-methoxy benzylthiosemicarbazone (p-MBTS) with Mn (II), Fe (II) and Co (II) metal ions. Structure of the ligand (2E)-2-(4-methoxybenzylidene)hydrazinecarbothioamide can be depicted as



(2E)-2-(4-methoxybenzylidene)hydrazinecarbothioamide

As is evident from the structure that these ligands contain nitrogen, sulphur and oxygen as donor atoms that are placed at equally favourable positions for chelation. On the basis of various spectral and magnetic studies it has been concluded that the ligand

(2E)-2-(4-methoxybenzylidene)hydrazinecarbothioamide is bidentate in nature. The effective magnetic moment (μ_{eff}) is used to determine the spin multiplicity of transition metal ions in the complexes³⁻⁴. This property is very effective in elucidating stereochemistry as well as coordination number of complexes. Donor set in the ligands helps in determining whether the metal ion is in High spin or low spin state.

The complexes of Mn(II), Fe (II) and Co (II) metal ions with this ligand are characterized by magnetic susceptibility measurements and electronic spectral studies. Magnetic moment of these complexes are compatible with high spin nature of these complexes in pseudo octahedral environment. Electronic spectra differentiate among four (square planar or tetrahedral), five (trigonal bipyramidal or square pyramidal) and six (octahedral or tetragonal) coordinated complexes of transition metals. Various assignments of bands have shown that prepared complexes are distorted octahedral. Ligand field theory has been applied to evaluate various ligand field parameters.

Aim of the Study

Preparation of some new complexes with chelating ligands for the study of their structure.

Review of Literature

Metal complexes of ligands having sulphur donor atoms were studied in 1965⁵. Later on metal complexes of sulphur nitrogen chelating agents were reviewed by Livingstone and Akbar Ali. They have laid special emphasis on the carcinostatic and antiviral activity of sulphur nitrogen ligands and their complexes. Metal complexes of thiosemicarbazones were studied by Campbell⁶. Thiosemicarbazone derivatives and their metal complexes have extensive biological properties such as antitumor⁷, fungicidal⁸, bactericidal⁹ and antiviral¹⁰ activities. Because of their biological activities, both as free ligands and in its metal complexes several studies have been made on the medicinal applications of thiosemicarbazone-based complexes¹¹⁻¹⁴. The main bulk of work in coordination chemistry is the complexes of transition metals. The distinct property of thiosemicarbazones is that it uses its sulfur atom of thioureido fragment for coordination, unlike isothiosemicarbazones where coordination takes place through the nitrogen atom of NH₂-group. Recently some copper(II) complexes with pyridoxal S-methylisothiosemicarbazone have been reported¹⁵.

Physical measurements and analytical techniques Microanalysis of Carbon, Hydrogen and Nitrogen

The ligands and their complexes were sent to research laboratory for the microanalysis of C, H, N contents.

Electronic Spectral Measurements

Electronic spectrum of the complexes were recorded in nujol mull on Beckman DMR-21 spectrophotometer in the region 300–1000 nm.

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Metal Estimation

Percentage of metals was determined by the standard method using EDTA as titrant. Complex was decomposed several times with dilute HNO₃ and residue was dissolved in water. Eriochrome black T was used as indicator.

Estimation of Sulphur and Halogens

Percentage of sulphur was estimated by standard method. Estimation of halogens was made by Volhard's method and ionisable chlorine was estimated as silver chloride.

Magnetic Measurements

For the measurement of magnetic susceptibility Gouy's technique was used on the powdered form of the complex at room temperature. Magnetic field was 1100 gauss and copper sulphate pentahydrate was used as calibrant. Assembly consisted of a semimicro balance and a leybolds electromagnet. Specimen tube was suspended from the pan with silver string.

Method of Calculation

Magnetic susceptibility using Gouy's balance is calculated using the formula

$$\beta = \frac{16.44 \times 10^{-6} \times \text{Room Temp. } ^\circ\text{K} \cdot W}{\text{Temp. } ^\circ\text{K} \cdot \Delta W's}$$

$$\Delta W's = (\Delta W - \delta_w)$$

δ_w = change in the weight of the empty tube

$\Delta W's$ = change in the weight of the calibrant

W = weight of the calibrant

$$\chi_g = \frac{\beta \times \Delta W_T}{W}$$

χ_g = gram susceptibility of the complex

β = Tube constant

W = weight of the complex

ΔW_T = Change in the weight of the complex

$$\mu_{\text{eff}} = 2.828 \sqrt{\chi_M} \times 10^6 \times T$$

μ_{eff} = Magnetic moment at temp. T

χ_M = molar susceptibility corrected for diamagnetism

T = absolute temperature

Racah's Parameters

Racah's interelectronic repulsion parameters B and C have been calculated using equation suggested by Lever and Figgis.

Experimental

Synthesis of the Ligand

One mole of hydrazinecarbothioamide was first dissolved in water and then to it 20 ml of glacial acetic acid was added. It was then heated on a water bath till a clear solution is obtained. To this clear solution one mole of para-methoxybenzaldehyde in ethyl alcohol is added. It was then refluxed on a steam bath for about one and half hour. On concentration white long needle like crystals were obtained. These were then recrystallized with ethyl alcohol several times. Yield was found to be about 75%. Analysis corresponds to the molecular formula C₉H₁₁N₃OS. The melting point of the compound was found to be 170°C.

Synthesis of the Metal Complexes

- Preparation of complex of Mn (II) metal ion : 100 ml (.05 mole) solution of the ligand was mixed with 50 ml (.05 mole) solution of metal chloride in ethyl alcohol. To this solution 1% alcoholic

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solution of NaOH was added to raise its pH upto 4.5. Then the solution was refluxed for about 2 to 3 hours. Mixture was then concentrated to reduce its volume to half and the precipitate obtained were filtered, washed with alcohol, acetone and ether and then dried.

- Preparation of complex of Fe (II) metal ion: 100 ml (.05 mole) ethanolic solution of the ligand was mixed with 50 ml (.05 mole) solution of ferrous chloride or ferrous thiocyanate in 50% ethyl alcohol. Dark brown precipitate formed is digested on water bath for an hour. The precipitate was then filtered and washed with alcohol, acetone and ether.
- Preparation of complex of Co (II) metal ion : 100 ml (0.02 mole) ethanolic solution of the ligand was mixed with 50 ml (0.02 mole) solution of cobalt salt. Reaction mixture was then refluxed for more than two hours on a water bath and then concentrated. on raising the pH up to 8 by adding 1% alcoholic KOH solution brown red precipitate were obtained. These were then digested, filtered and washed with ethanol and ether and were finally dried in a vacuum dessicator.

Result and Discussion

Complex of Mn (II) Metal Ion

Magnetic and spectral studies of Mn (II) complexes with many ligands have shown octahedral geometry¹³⁻¹⁴ in majority of cases while a few tetrahedrally coordinated complexes have also been reported¹⁵. In the present studies the complex of Mn(II) with (2E)-2-(4-methoxybenzylidene)hydrazinecarbothioamide has been found to be pseudooctahedral by the help of magnetic studies. The Analyses corresponds to the molecular formula [Mn (C₉H₁₁N₃OS)₂ Cl₂] (Table 1). The complex is stable upto 250°C. Magnetic moment of the complex at room temperature is 5.80 (Table 2) which is well in range generally observed for high spin Mn (II) complexes. Electronic spectra shows four bands in the regions 18500 cm⁻¹, 22200 cm⁻¹, 26850 cm⁻¹ and 31300 cm⁻¹. These bands can be assigned to sextet-quartet transitions ⁴T_{1g}(G), ⁴T_{2g}(G), ⁴E_g(G), ⁴A_{1g}(G) from the ground state ⁶A_{1g} respectively. Values of B, C and Dq are given in table 2.

Complex of Fe (II) Metal Ion

Fe(II) forms a number of complexes which are found to have a distorted octahedral geometry. Data regarding the Fe(II) complexes is very little¹⁶. Yield of the complexes of Fe(II) with (2E)-2-(4-methoxybenzylidene)hydrazinecarbothioamide has been found to be approximately 65% and The Analyses corresponds to the molecular formula [Fe(C₉H₁₁N₃OS)₂X₂] where X = Cl, CNS (Table 1). The magnetic moment observed are 5.25 and 5.80

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respectively at room temperature. The value is slightly lower than that reported for high spin octahedral Fe(II) complexes. This may be due to the lowering of symmetry effect or delocalisation of electrons¹¹. Electronic spectra of Fe (II) complexes shows two bands in the regions 8600 cm⁻¹ and 10500 cm⁻¹ that can be assigned to ⁵T_{2g} → ⁵E_g transition may be arising by the split of ⁵E_g band. Splitting may be due to Jahn teller distortion in the present case. Actual amount of distortion cannot be calculated however McClure molecular orbital parameter dσ can be calculated by the fact that splitting of the band is 8/3 dσ and sign of parameter is selected on the basis whether inplane ligand is having greater strength or out of plane ligand is having greater strength (table 2).

Complex of Co (II) Metal Ion

The cobalt (II) ion which has 7 electrons is best known for four coordinated tetrahedral and six coordinated octahedral stereochemistry¹⁷. The cobalt (II) complexes of sulphur donor ligand exhibit anomalous magnetic behaviour¹⁸. Complex of Co (II) with pMBTSC was blue in colour and yield of the product has been found to be approximately 70%. The Analyses corresponds to the molecular formula [Co (C₉H₁₁N₃OS)₂ X₂] where X = Cl, Br, I, NO₃ (Table 1). The stoichiometric ratio for the brown coloured complex comes out to be 1:2. The magnetic moment values observed for various Co(II) complexes is 4.50 to 4.85 B.M respectively (table 3) which is slightly less than that observed for high spin octahedral cobaltous complexes and may be attributed to incomplete quenching of the orbital contribution to the magnetic moment. Three spin allowed bands are expected corresponding to the transitions ⁴T_{1g}(F) → ⁴T_{2g}(F), ⁴T_{1g}(F) → ⁴A_{2g}(F), ⁴T_{1g}(F) → ⁴T_{1g}(P). The ⁴A_{2g} state is derived from (t_{2g})³(e_g)⁴ configuration while ⁴T_{1g}(F) state is derived mainly from (t_{2g})⁵(e_g)². Hence ⁴T_{1g}(F) → ⁴A_{2g}(F) transition is much weaker than others. Electronic spectra consists of two main bands - a broad band in the region 9650-10140 cm⁻¹ and a strong band between 20000-20150 cm⁻¹ with two shoulders appearing between 17850-18080 cm⁻¹ and 18220-19840 cm⁻¹. Lowest and highest bands of energy can be assigned to v₁ and v₂ transitions and shoulders may be due to splitting of v₃ in many components or may be because of the appearance of v₂ transition. 10 Dq and B were calculated to be 12060-12160 and 848-861 cm⁻¹. Ratio of v₂ / v₁ falls in the range 1.92-2.00 (table 3) suggesting the shoulder 18540-20150 cm⁻¹ to be due to v₂ transition. Since the Dq independent spin forbidden transitions to ²T₁ and ²T₂ components of ²G state can also occur in this region at the energy slightly lower than above transition, the shoulder of lower energy 17850-18080 cm⁻¹ may be attributed to ⁴T_{1g}(F) → ²T_{1g}, ²T_{1g} transition.

Table 1: Analytical data of the complexes of Mn (II), Fe (II) and Co(II)

complex	Calculated percentage						Found percentage					
	M	C	H	N	S	X	M	C	H	N	S	X
[Mn (C ₉ H ₁₁ N ₃ OS) ₂ Cl ₂]	10.11	39.78	4.05	15.45	11.82	13.05	10.24	40.02	4.12	15.98	11.9	12.98
[Fe (C ₉ H ₁₁ N ₃ OS) ₂ Cl ₂]	10.25	39.67	4.06	15.42	11.76	13	10.22	39.72	4.12	15.61	11.2	13.02
[Fe (C ₉ H ₁₁ N ₃ OS) ₂ (CNS) ₂]	9.45	40.68	3.76	18.97	21.72	-----	9.55	40.91	3.78	18.96	21.7	-----
[Co (C ₉ H ₁₁ N ₃ OS) ₂ Cl ₂]	10.75	39.43	4.05	15.33	11.69	12.93	10.85	39.56	4.07	15.33	11.72	12.94
[Co (C ₉ H ₁₁ N ₃ OS) ₂ Br ₂]	9.25	33.92	3.47	13.19	10.07	25.08	9.33	33.93	3.48	13.19	10.08	25.03
[Co (C ₉ H ₁₁ N ₃ OS) ₂ I ₂]	8.06	29.56	3.04	11.49	8.77	34.71	8.09	29.62	3.06	11.52	8.89	34.82
[Co (C ₉ H ₁₁ N ₃ OS) ₂ (NO ₃) ₂]	9.82	35.95	3.69	18.64	10.62	-----	9.88	35.87	3.72	18.8	10.72	-----

Table 2 : Magnetic and electronic spectral data of the complexes of Mn (II) and Fe (II)

Complex	Observed bands cm ⁻¹	Assignments	Dq (L) cm ⁻¹	B cm ⁻¹	C cm ⁻¹	μ _{eff} B.M (298 ^o C)
[Mn(C ₉ H ₁₁ N ₃ OS) ₂ Cl ₂]	18500 22200 26850 31300	⁶ A _{1g} → ⁴ T _{1g} (G) ⁶ A _{1g} → ⁴ T _{2g} (G) ⁶ A _{1g} → ⁴ E _g (G) ⁶ A _{1g} → ⁴ A _{1g} (G)	11452	881	3524	5.80
[Fe(C ₉ H ₁₁ N ₃ OS) ₂ Cl ₂]	8600 10500	⁵ T _{2g} → ⁵ E _g Charge transfer	dσ 1050	713		5.25
[Fe(C ₉ H ₁₁ N ₃ OS) ₂ (CNS) ₂]	8500 10750	⁵ T _{2g} → ⁵ E _g Charge transfer	1075	844		5.30

Table 3 : Magnetic and electronic spectral data of the complexes of Co (II)

Complex	Observed bands cm ⁻¹	Assignments	Dq cm ⁻¹	v ₂ / v ₁	Racah's parameter cm ⁻¹	μ _{eff} B.M (298 ^o C)
[Co(C ₉ H ₁₁ N ₃ OS) ₂ Cl ₂]	9650 18540 20150 17800	⁴ T _{1g} (F) → ⁴ T _{2g} (F) ⁴ T _{1g} (F) → ⁴ A _{2g} (F) ⁴ T _{1g} (F) → ⁴ T _{1g} (P) ⁴ T _{1g} (F) → ² T _{1g} , ² T _{1g}	1206	1.92	861	4.50
[Co(C ₉ H ₁₁ N ₃ OS) ₂ Br ₂]	9675 18690 20000 17730	As above	1209	1.93	855	4.62
[Co(C ₉ H ₁₁ N ₃ OS) ₂ I ₂]	9690 18980 20130 17950	As above	1211	1.95	857	4.72
[Co(C ₉ H ₁₁ N ₃ OS) ₂ (NO ₃) ₂]	9730 19480 20020 18070	As above	1216	2.00	848	4.85

Conclusion

Based on various physicochemical data's and electronic spectral studies discussed as above distorted octahedral geometry has been proposed for the Mn (II) and Fe (II) and Co(II) complexes. All the complexes are found to have 1:2 stoichiometry. Magnetic moment of the prepared complexes is consistent with their high spin nature in pseudooctahedral environment. Ligand behaves as bidentate. Pharmacological studies of these complexes may provide some biologically important results because ligands are biologically active.

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