

Synthesis and Characterisation of Some Complexes of Co(II) Metal with Schiff Base

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Abstract: *In this paper, we present about the synthesis and characterisation of some complexes of Co(II) metal with Schiff base. The complexes of Cobalt(II) cation have been prepared with Schiff base ligand, benzophenonesemicarbazone in the presence of bases having nitrogen and oxygen atoms as their donor sites. The general formulae of the complexes have been found to be $[Co(L)_2(B)_2]$ where L = ligand and B = bases. On the characterisation of the ligand and the complexes by usual physico-chemical methods, all the complexes have been found to be mono-meric, non-electrolyte, paramagnetic and octahedral in geometry.*

Keywords: Synthesis, Ligand, Complex, Paramagnetic, Octahedral, Geometry, Schiff Base.

1. Introduction

A large amount of research work has been carried out for the formation of complexes of divalent transition metals with Schiff bases having nitrogen and oxygen atoms as their donor sites. But least research work has been carried out with Schiff bases containing semicarbazide in its moiety. Therefore, in this paper, we have undertaken to report the formation of complexes of Cobalt(II) cation with benzophenonesemicarbazide in presence of bases like water, ammonia, quinoline, phenyl isocyanide, pyridine and π -picolene.

2. Experimental

2.1 Preparation of Ligand BenzophenoneSemicarbazone :

A suspension of 2.0g (0.01 mole) in minimum volume of ethylalcohol was allowed to react with semicarbazide hydrochloride, 1.2g (0.01 mole) dissolved in 10% ethanolic solution of sodium acetate. The resulting mixture was shaken well. Then it was heated for about three hours on a water bath with regular shaking. On cooling the solution under ice-bath, a faint yellowish precipitate was obtained. The precipitate thus obtained was separated by filtration. Then it was washed with aqueous ethanolic solution, dried and crystallised with methyl alcohol. A faint yellowish solid was obtained with melting point ± 2 , 180°C. The compound was further analysed and found to contain carbon = 69.72%, hydrogen = 5.45%, nitrogen = 17.60% which corresponds the molecular formula $C_{14}H_{13}N_3O$. The identification of the compound was further confirmed by spectroscopy.

2.2 Preparation Of Co(Ii) Complexes :

4.76g (0.01 mole) of the ligand was completely dissolved in a minimum volume of ethyl alcohol 2.35g (0.01 mole) of Cobalt(II) chloride hexahydrate was also completely dissolved in aqueous thanolic solution. Both the solution were mixed together gradually. Then the resulting solution was shaken well and heated under reflux on water bath for about two hours when a pinkish brown solid was obtained in the solution. The solid was separated by filtration and washed with a small amount of ethyl alcohol followed by ether and dried over KOH pellets placed in a desiccator.

Similarly, the complexes of Co(II) cations were prepared separately with the ligand and the bases like ammonia, quinoline, phenylisocyanide, pyridine and α -picoline. The molar ratio of the metal and the ligand was always maintained 1:2 respectively in each case. The solids were obtained with slight variation in their colours for different bases. On characterisation by usual physico-chemical methods, the complexes were found to be mon-meric, non-electrolyte, paramagnetic and octahedral in nature with general molecular formulae $[\text{Co}(\text{L})_2(\text{B})_2]$ where L = ligand and B = bases.

2.3 Analytical Table Of Co(Ii) Complexes With The Ligand And Different Bases, Found \rightarrow % And (Calculated \rightarrow %)

S.N.	Compounds	Metal	Carbon	Hydrogen	Nitrogen
1.	$[\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O})_2(\text{H}_2\text{O})_2]$	11.42 (11.96)	58.10 (58.41)	4.94 (4.92)	11.30 (11.24)
2.	$[\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O})_2(\text{NH}_3)_2]$	9.24 (9.76)	58.34 (58.65)	5.32 (5.30)	19.75 (19.70)
3.	$[\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O})_2(\text{C}_9\text{H}_7\text{N})_2]$	6.82 (7.18)	69.10 (69.33)	4.82 (4.81)	14.20 (14.13)
4.	$[\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O})_2(\text{C}_6\text{H}_5\text{NC})_2]$	7.46 (7.94)	67.70 (68.02)	4.60 (4.58)	15.16 (15.11)
5.	$[\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O})_2(\text{C}_5\text{H}_5\text{N})_2]$	7.96 (8.32)	64.92 (65.28)	4.94 (4.92)	16.24 (16.18)
6.	$[\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O})_2(\text{C}_5\text{H}_4\text{NCH}_3)_2]$	7.82 (8.17)	66.14 (66.58)	5.30 (5.27)	15.62 (15.55)

which corresponds to the molecular formulae $\text{Co}(\text{L})_2(\text{B})_2$ where L = ligand and B = bases.

2.4 Chemical Required :

Cobalt(II) acetate/chloride, ethyl alcohol, ether, DMF, ammonia, quinoline, phenyl isocyanides, pyridine, α -picoline, ether, methyl alcohol.

All the chemicals taken for the present research work were obtained either from E-Merck pure or BDH (AR) quality. They were used without further purification.

3. Analytical Methods

3.1 Cobalt :

The compound was ignited for a few minutes, cooled and then treated with *conc.* HNO_3 acid by which residual cobalt is oxidised and the oxide of cobalt can be converted into nitrate. The product was heated to expel out excess of nitric acid. Finally excess of *conc.* H_2SO_4 was added to convert the nitrate into sulphate and then heated between 450°C - 500°C and determined as CoSO_4 by weighing.

3.2 Hydrogen, Carbon and Nitrogen:

The estimation of carbon, hydrogen and nitrogen were done by semi-micro combustion method.

3.3 Conductivity Measurement:

Electrical conductivity of the solutions of complexes were completed by conductivity under bridge manufactured by Wiss-TechenWerchStathen type - LBR at room temperature in DMF. Pure DMF was used as solvent and N/10 and N/100 solutions as cell constant at room temperature.

3.4 U.V. : Visible Spectra Photometric Measurements :

The electronic absorption spectra of the complexes were recorded on Hitachi-320 spectrophotometer.

3.5 I.R. Spectra :

The infra-red spectra were recorded on Perkin Elemer-577 spectrophotometer using KBr pellets in

the range of 4000-400 cm^{-1} .

3.5 Magnetic susceptibility :

The measurement of magnetic susceptibility of the complexes were determined by Gouy's method by using $[\text{HgCo}(\text{SCN})_4]$ as calibrant.

4. Results and Discussion

The values of electrical conductivity for all the Cobalt(II) complexes obtained in the range of 12 to 18 indicate non-electrolyte nature of all the complexes.

The values of magnetic moment obtained in the range of 4.92 to 5.10BM suggest unambiguously octahedral geometry for all the complexes.

An unsymmetrical and broadband obtained about 23,500 cm^{-1} due to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transition indicates octahedral nature of all the complexes.

4.1 Comparison of I.R. spectra of the ligand and the complexes:

Comparison of I.R. spectra of the ligand and the complexes to decide the bonding sites of the ligand and the structure of the complexes. Although I.R. spectra of all the complexes are quite complex. But the band positions obtained due to the vibrations of $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{O})$, $\nu(\text{C}-\text{O})$, $\nu(\text{N}-\text{H})$, groups are appreciably changed after complex formation. The absence of a strong band about 1860 cm^{-1} in the ligand molecule indicates that the ligand molecule is prone to form complexes in the enolic form. In some cases, the bands obtained at 3380 cm^{-1} due to the vibrations of hydroxy -OH group, indicating that strong hydrogen bonding present in the ligand molecule has been broken down and one -NH group are present even after complex formation. A medium and sharp band obtained in the range of 1510-1530 cm^{-1} in the ligand molecule due to the vibrations of >C-OH group have been shifted to 1540-1550 cm^{-1} in the complexes.

The increase in the band position (increase in the bond length) indicates the deprotonation of -OH group of hydrazine group.

The deprotonation of -OH group and participation of oxygen atom in the complex formation of -OH group has been further confirmed by the appearance of a new band in the range of 530-550 cm^{-1} due to the vibration of (M-O) bond in the complexes.

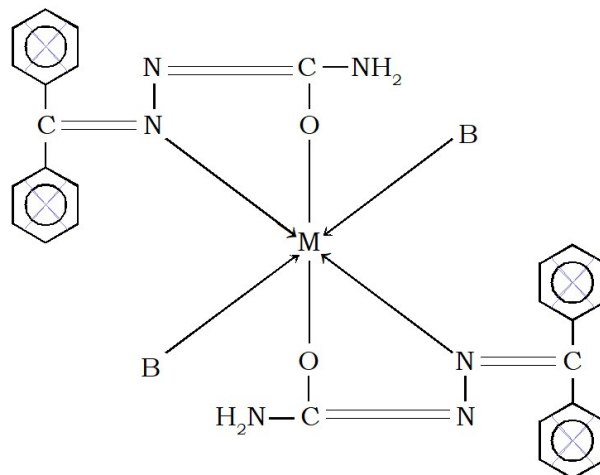
A strong and broad band obtained in the range of 1640-1650 cm^{-1} in the ligand molecule has been reduced by 50-60 cm^{-1} in the complexes indicating the participation of aldimino or azomethine nitrogen (>C=N-) in the complexes.

The coordination through aldimino nitrogen has been further confirmed by the appearance of a band obtained in the range of 420-430 cm^{-1} due to the vibrations of (M-N) bond in the complexes.

Thus aldimino nitrogen and oxygen atom of -OH group are the bonding sites of the ligand molecule. Thus ligand molecules behave as mono-anionic bi-dentate molecule. Two molecules of the ligand satisfied two primary and two secondary valencies of the Cobalt(II) cation and remaining two valencies are satisfied by the bases having oxygen and nitrogen atoms as their donor sites.

In case of aquo and amine complexes, no two separated bands are obtained for coordinating H_2O and NH_3 molecules but a strong and broad band at around 3430 cm^{-1} due to the overlapping of the two bonds by coordinated H_2O and NH_3 molecules in complex formation. In case of phenyl isocyanide complexes, there is increase in the (C=N) vibrations of the ligand (2160 cm^{-1}) and the complexes (2210 cm^{-1}) indicating the involvement of isocyanide (N-C) group in complex formation. In case of quinoline, pyridine and α -picoline, the bands obtained at about 1440 cm^{-1} , 990-1040 cm^{-1} and 500-520 cm^{-1} in the complexes indicate the participation of quinoline, pyridine and α -picoline in the bond formation with the metal cation.

Thus on the basis of elemental analysis, measurement of electrical conductivity, magnetic moments, electronic transition and I.R. spectra, the complexes of Cobalt(II) metals with the ligand in the presence of bases like water, ammonia, quinoline, phenyl isocyanide, pyridine and α -picoline has been suggested to be non-electrolyte, mono-meric, paramagnetic and octahedral in geometry with general formula $[\text{Co}(\text{L})_2(\text{B})_2]$.



where M = Cobalt(II) Cation
 L = Benzophenonesemicarbazone
 B = water, ammonia, quinoline, phenyl isocyanide,
 pyridine and α -picoline.

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References:

1. H. Schiff : *Annual Phys*, 150(1869), 193.
2. P. G. Mann and B. C. Saunders : *Practical Organic Chemistry*, 4th Edition, 1960.
3. John Dyer : *Application of Absorption Spectroscopy of Organic Compounds*, Prentice/Hall of India Private limited, New Delhi, 1974.
4. PushpaKumariet. al. : *IJRAR*, 6(2019), 616-617.
5. PallweeKumariet. al. : *IJRAR*, 6(2019), 618-619.
6. B. N. Piggis : *Introduction to Ligand Field*, Willey Eastern, New York (1976).
7. K. Nakamoto : *"Infrared and Raman Spectra of Inorganic and Coordination Compounds"*, John Willey and Sons Inc., New York (1979).
8. L. J. Bellarry : *Infrared Spectra of Complex Molecules*, John Willey and Sons Inc., New York, 64(1957).
9. SudhanshuRajaket. al. : *J. Chemtracks*, 20(208)63-66.
10. D. G. Palke, S. D. Salemke and B. K. Ray : *Asian J. Chem.*, 29(2017)2707-2710.
11. Anand Mohan Jha : *J. Biol. Chem. Chron.*, 2018, 4(3), 07-12.