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Synthesis and Characterization of S-Methyl-β-N-(4-NN-Bis 2'-Chloroethylaminephenylmethylene)Dithiocarbazate Schiff Base and its Metal Complexes with Co(II) and Ni(II) ion.

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ABSTRACT

The titled Schiff base (benzme) was synthesized by the condensation of S-methyl dithiocarbazate with benzaldehyde mustard in a 1:1 molar ratio. Dark yellow crystals of the Schiff base was formed. General formula of Schiff base being $C_{13}H_{17}N_3S_2Cl_2$ and m.p. was found to be 180°C. The Schiff base reacts with divalent metal ions(Co(II) and Ni(II)) to form the neutral metal complex $[Co(benzme)_2]$ & $[Ni(benzme)_2]$. The Schiff base and their metal complexes have been characterized by a variety of physico-chemical techniques, viz. elemental analyses, IR, Mass, ^{1}HNMR and electronic spectral studies. The Schiff base behaved as uninegatively charged bidentate ligand. IR and ^{1}HNMR spectral evidence indicate that the Schiff base coordinates to the Co(II) and Ni(II) ion via the azomethine nitrogen atom and the thiolo sulfur atom.

Keywords: S-methyldithiocarbazate, benzaldehyde mustard, Schiff base

1. Introduction:

Schiff bases formed by the condensation of S-methyldithiocarbazate and carbonyl compounds contain nitrogen and sulfur donor atoms and consequently Schiff bases are capable of forming stable complexes with a wide variety of metal ions[1-10] and many of these Schiff bases have been shown to exhibit interesting physico-chemical properties[11-12]. We report here the synthesis and spectroscopic characterization of benzaldehyde mustard Schiff base of S-methyldithiocarbazate together with the structure of their Co(II) and Ni(II) complexes.

2. Experimental:

All chemicals and solvents used in the experiment were of reagent grade and were used without further purification.

2.1. Preparation of S-methyldithiocarbazate (SMDTC):

Potassium hydroxide (22.8g) was completely dissolved in 9:1 alcohol–water mixture (140 ml) and the mixture was cooled in ice. To the cooled solution hydrazine hydrate (20g) was added slowly with constant stirring. A solution of carbon disulphide (30.4g) in alcohol (25 ml) was then added drop wise from dropping funnel with constant stirring over a period of one hour. The temperature of the mixture was kept below 10°C. After one hour two layers were formed. The yellow oily (lower) layer was then separated using a separating funnel and dissolved in previously cooled 40% ethanol (60 ml). The mixture was kept

in ice bath and methyl iodide (58g) was added slowly with vigorous mechanical stirring. After this, the mixture was stirred for further 10 min. when a white product was separated out. Ice cooled water (100 ml) was then added and the stirring was continued for 10 min. The product was filtered off, washed with water and then dried in air. The crude product was recrystallized from ethanol and dried in vacuum over anhydrous $CaCl_2$ in a desiccator. Yield, 40% and melting point 81°C were recorded.

2.2. Synthesis of the S-methyl-β-N-(4-NN-bis 2'-chloroethylaminephenylmethylene)di-thiocarbazate (benzme):

S-methyldithiocabazate (1.220g) (0.01 mol.) was dissolved in hot absolute ethanol (15 ml.). This was added to a solution of benzaldehyde mustard (2.460g) (0.01 mol.) in ethanol (15 ml.) in 1:1 molar ratio. Light yellow colour was obtained. The mixture was heated on a water bath and refluxed for 25 minutes when crystals started appearing. Then refluxing was stopped and the reaction mixture was allowed to stand overnight whereupon the dark yellow crystals which had formed were filtered off, the Schiff base was purified by recrystallized from ethanol and dried in vacuum over anhydrous $CaCl_2$ in a desiccator. Yield, 70.65%, And melting point 180°C. were recorded. Anal. Found: C, 44.57%; H, 4.86%; N, 12.00%; S, 18.29%; Cl, 20.29%; Found: C, 44.33%; H, 4.23%; N, 12.33%; S, 18.11%; Cl, 20.11%, Calc. For was $C_{13}H_{17}N_3S_2Cl_2$.

^{1}H NMR: 2.68 ppm ($-SCH_3$), 10.13 ppm (-NH), 7.76 ppm (-CH=N-).

2.3. General method of preparation of the complexes:

The Schiff base (0.002 mol) was dissolved in hot absolute ethanol (20 ml.). This was added to a solution of metal (0.001 mol) in ethanol (07 ml.) in 2:1 ratio. Dark colour was obtained. The mixture was heated on a water bath and refluxed for some time when crystals started appearing. Then refluxing was stopped and the reaction mixture was allowed to stand overnight whereupon crystals were formed. Precipitate was filtered off and the complex was purified by recrystallization from ethanol and dried in vacuum over anhydrous $CaCl_2$ in a desiccator. Yield…..; MP. . ….

2.4. Preparation of Bis[S-methylβ-N-(4-NN-bis 2'-chloroethylaminephenylmethylene) dithiocarbazato]cobalt(II): [Co^{II}(benzme)$_2$]

S-methyl-β-N-(4-NN-bis 2'-chloroethylaminephenylmethylene)dithiocarbazate (0.700g) (0.002 mol.) was dissolved in hot 90% ethanol (20 ml.). This was added to a solution of cobalt acetate tetrahydrate (0.250g) (0.001 mol.) in 90% ethanol (10 ml.) in 2:1 molar ratio. Deep brown colour was obtained. The mixture was heated on a water bath and refluxed for about 03 minutes when crystals started appearing. Then refluxing was stopped and the reaction mixture was allowed to stand overnight whereupon deep brown crystals were formed. Precipitate was filtered off and the complex was purified by recrystallization from ethanol and dried in vacuum over anhydrous $CaCl_2$ in a desiccator.

Yield, 75% and melting point 260°C were recorded. Anal. Found: C, 41.22%; H, 4.23%; N, 11.10%; S, 16.91%; Cl, 18.76%; Co, 7.79%; Found: C, 40.77%; H, 4.05%; N, 10.86%; S, 16.30%; Cl, 18.19%; Co, 7.15%.

2.5. Preparation of Bis[S-methyl-β-N-(4-NN-bis 2'-chloroethylaminephenylmethylene) dithiocarbazato] nickel(II): [Ni^{II}(benzme)$_2$]

S-methyl-β-N-(4-NN-bis 2'-chloroethylaminephenylmethylene)dithiocarbazate (0.700g) (0.002 mol.) was dissolved in hot absolute ethanol (20 ml.). This was added to a solution of nickel nitrate hexahydrate (0.290g) (0.001 mol.) in ethanol (10 ml.) in 2:1 molar ratio. Deep brown colour was obtained. The mixture was heated on a water bath and refluxed for about 03 minutes when crystals started appearing. Then refluxing was stopped and the reaction mixture was allowed to stand overnight whereupon golden brown crystals were formed. Precipitate was filtered off and the complex was purified by recrystallization from ethanol and dried in vacuum over anhydrous $CaCl_2$ in a desiccator.

Yield, 85% and melting point 260°C were recorded. Anal. Found: C, 41.27%; H, 4.23% ; N, 11.11%; S, 16.93%; Cl, 18.78%; Ni, 7.67%; Found: C, 40.88%; H, 4.11%; N, 10.87%; S, 16.23%; Cl, 18.28%; Ni, 7.17%.

Table-1

Yield, colour, melting point and elemental analysis of synthesized compounds.

Compounds	Yield (%)	Colour	MP. (°C.)	Found (Calculated) (%)			
				C	H	N	S
benzme	70.65	Dark Yellow	180	44.57 (44.33)	4.86 (4.23)	12.00 (12.33)	18.29 (18.11)
$[Co(benzme)_2]$	75	Deep brown	260	41.22 (40.77)	4.23 (4.05)	11.10 (10.86)	16.91 (16.30)
$[Ni(benzme)_2]$	85	Golden brown	260	41.27 (40.88)	4.23 (4.11)	11.11 (10.87)	16.93 (16.23)

2.6. Physical measurements:

Infrared spectra were recorded on a Perkin-Elmer RX1 FT-IR spectrometer using KBr pellets in the 4000-400 cm^{-1} region. Elemental analyses were carried out using a Elementar Vario EL III Carlo Erba 1108 spectrometer. ^1H NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer in DMSO using TMS as the internal standard. Mass spectra were recorded on a Thermo Finnigan LCQ Advantage maxion trap mass spectrometer. Electronic absorption spectra of the Schiff base and complexes were obtained on a UV-2450 spectrophotometer using DMSO solution in the range 200-600 nm. An Electro-thermal digital melting point apparatus was used to determine the melting points.

3. Results and Discussion:

The Schiff base was obtained by reacting S-methyldithiocarbazate with benzaldehyde mustard in a 1:1 molar ratio. The ligand has a proton adjacent to the thione group and consequently, they are capable of existing either as the thioketo form (IA) or enethiol form (IB) or a mixture of both the thioketo and thioenol forms.

3.1. Infrared spectra:

The IR Spectrum of the Schiff base (benzme) in KBr do not display the (S-H) band at around 2700 cm^{-1} but show (N-H) at 3203 cm^{-1} indicating that in the solid state they remain as the thioketo form IA. The (N-H) band present in the Schiff base was not observed in any of the two metal complexes, indicating deprotonation of the Schiff base in situ to form the thiol tautomers for the formation of metal complexes to take place. The (C=S) band at 1095 cm^{-1} for Schiff base was also not observed in the metal complexes, thus supporting the suggestion of coordination through the thione sulfur[13]. Sharp bands observed in the spectrum of the Schiff base at approximately at 1608 cm^{-1} are assigned to (C=N)· In metal complexes this absorption was shifted to lower frequencies indicating coordination of the azomethine nitrogen to the central metal atoms[14-16]. The lowering in frequency of the (N-N) band in all the metal complexes is another clear indication that the coordination involves azomethine nitrogen[17].

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Table-2

Selected IR bands and electronic spectral data for (benzme) and its copper(II) & nickel(II) complexes.

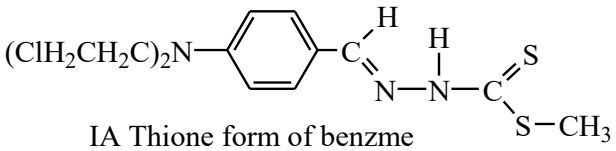
Compounds	**IR bands**				**Electronic spectral data**
	ν(N-H)	*ν*(C=N)	*ν*(N-N)	*ν*(C=S)	λmax (nm)
benzme	3101	1608	1176	1095	
$[Co(benzme)_2]$	-	1571	1018	-	410, 280, 260
$[Ni(benzme)_2]$	-	1640	769	-	430, 380, 260

3.2. H^1 NMR spectra:

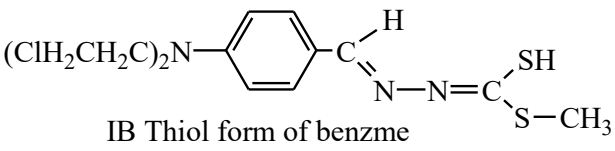
The H^1 NMR spectra of Schiff base in $CDCl_3$ do not exhibit any signal at approximately 4 ppm due to S–H proton, however, they displays at δ = 7.76(s) ppm, which is assignable to one protons on azomethine carbon (HC=N-). The three protons of $–SCH_3$ which are more shielded than HC=N- protons, hence peak at δ = 2.68(s) ppm is assigned to it which is a singlet. The two aromatic protons adjacent to amino group are more deshielded than other two aromatic protons of the benzene ring hence these two protons appeared as doublet at down field; at δ = 7.63-7.66(d) ppm. the remaining two aromatic protons which are less deshielded appeared as doublet at higher field; at δ = 6.70-6.73 ppm. A signal at δ = 3.83 ppm. is due to azoethine protons.

A very small peak appeared at δ = 1.59(s) ppm in the thiol proton (–SH) and a peak at δ = 10.13 ppm is due to –NH proton. The presence of both the groups in ligand indicates that in solution the ligand molecule exits in the following two tautomeric forms

(Fig: 1)



IA Thione form of benzme



IB Thiol form of benzme

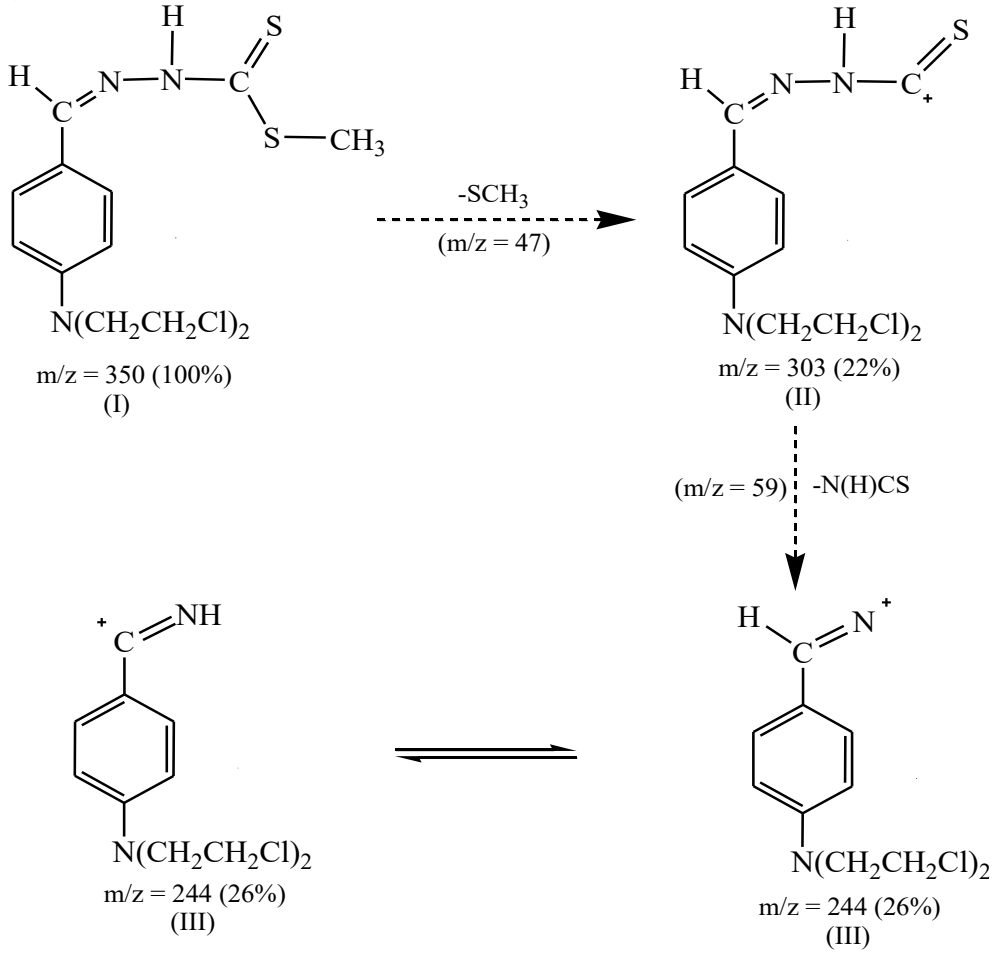
Fig. 1. The Thione and thiol forms of the Schiff base of S-methyl-β-N-(4-NN-bis 2'-chloroethyl-aminephenylmethylene)dithiocarbazate Schiff base

3.3. Mass spectra:

he mass fragmentation patterns of the title Schiff base molecule are compatible with the proposed molecular formula of $C_{13}H_{17}N_3S_2Cl_2$.

The molecular ion peak (I) appears at m/z: 350 (100%) and a peak at m/z: 352 (74%) is assignable to M+H]+2 peak, which is a characteristic peak due to presence of two isotopes of chlorine atom with in the molecule. The molecular ion (I) by loss of the radical SCH_3 (m/z: 47) gives the ion (II), m/z: 303 (22%) which by loss of the radical N(H)CS (m/z: 59) gives the ion (III), m/z: 244 (26%).

The probable mechanism of mass fragmentation of the Schiff base is given below:



3.4. Electronic spectra:

The electronic spectral data of the synthesized compounds are shown in Table 2. The electronic spectra of the Schiff base display band in the 380 nm range which can be assigned to *n* π* transition of the azomethine group[18]. The UV-VIS spectra of Co(II) complex (d^7configuration) indicated a distorted tetrahedral structure. The $^4A_2(F)$ $^4T_2$ band can be seen at 410 nm. for (benzme) complex. The band at 280 nm. for Co(II) complex can be assigned to the $^4A_2$ $^4T_1$ and the band at 260 nm. for Co(II) complex can be assigned to the A_2 $^3T_1(P)$ transition[19-20]. The electronic spectra of the Ni(II) complex at 430, 380, 260 nm was characteristic of a square planar Ni(II) configuration[21]. The band may be attributed to the ^1A_1g ^1A_2g, ^1A_1g ^1B_1g and ^1A_1g ^1E_1g transition. The appearance of this LMCT band in the electronic spectra of the nickel(II) complex is a strong evidence that the nickel(II) ion is coordinated to the Schiff base via the sulfur atom. Such S M(II) LMCT bands have also been observed in the electronic spectra of nickel(II) complex of dithiocarbazate. In the spectra of mono-ligated nickel(II) complex, a d-d band is observed at approximately 380 nm which is similar to that observed in other spuare-planar nickel(II) complex NS bidented ligand. [Ni(benzme)$_2$] complex adopts a distorted square planar structure.

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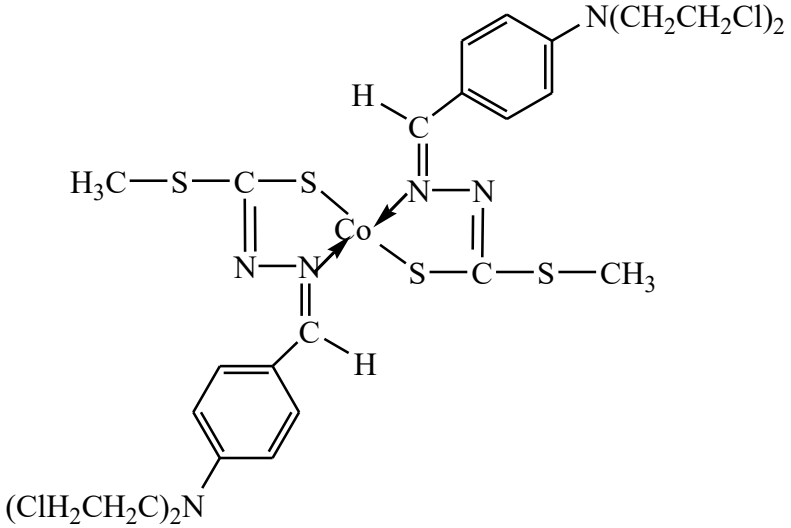

Fig. 2. The structure of [Co(benzme)$_2$] complex.

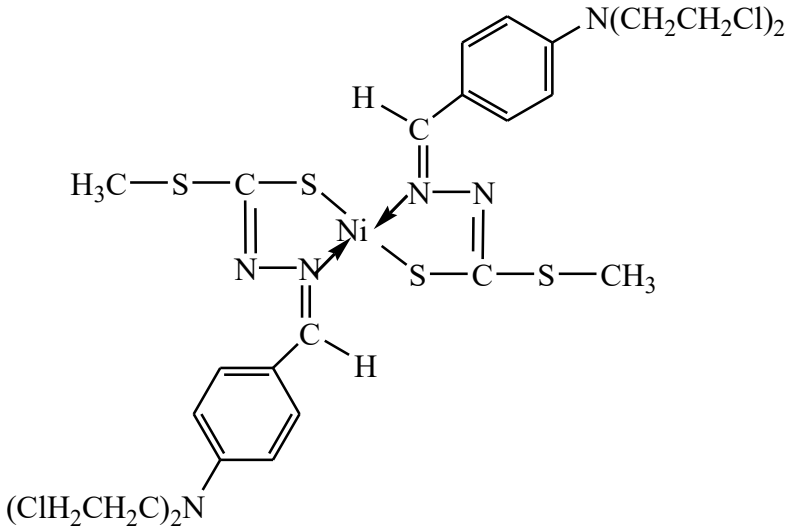

Fig. 3. The structure of [Ni(benzme)$_2$] complex.

4. Conclusion:

The Schiff base behave as unine-gatively charged bidentate ligand with Co(II), Ni(II) complexes. The IR spectra of the free ligand indicate that in solid state the ligand remains in the thione form. The (N-H) band present in the Schiff base was not observed in any metal complexes, indicating deprotonation of the Schiff base in situ to form the thiol tautomers for the formation of metal complexes to take place. The (C=S) band at 1095 cm^{-1} for Schiff base was also not observed in the metal complexes, thus supporting the suggestion of coordination through the thione sulfur. The thione and thiol tautomeric forms may be expected to exist in solution but the H^1 NMR spectra of Schiff base indicate that the ligand even in solution, exist predominantly as the thione tautomers. The UV-VIS spectra indicated that [Co(benzme)$_2$] complex has a tetrahedral geometry and [Ni(benzme)$_2$] complex has a square planar geometry.

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