



Studies of Distorted Octahedral Complexes of Cobalt, Nickel and Copper and Their Antibacterial Properties

VIJAY KUMAR¹, RAJIV KUMAR SINGH², VEENA KUMARI³,
BIRENDRA KUMAR^{4*} and SHIVADHAR SHARMA³

¹P. G. Department of Chemistry, Raj Narayan College, Hajipur-84410, India.

²P. G. Department of Chemistry, Tej Narayan Banaili College, Bhagalpur-812007, India.

³P. G. Department of Chemistry, M.U. Bodh-Gaya-824234, India.

⁴Department of Chemistry, J.J. College, Gaya (M.U)-823003, India.

*Corresponding author E-mail: birendra5556@gmail.com

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ABSTRACT

The ligand, 3-hydroxy-4-methoxybenzaldehydethiosemicarbazone has been prepared by the condensation of 3-hydroxy-4-methoxybenzaldehyde and thiosemicarbazide. With the help of this ligand the complexes of Co(II), Ni(II) and Cu(II) have been prepared with general formula $[ML_2X_2]$ where X is secondary ligand, Cl^- , NO_3^- and CH_3COO^- . The composition of complexes has been established by their microanalysis, while the metal contents have been determined gravimetrically and volumetrically. On the basis of IR spectra, the coordinating mode of ligand has been determined and has been found to have coordinated through azomethine nitrogen and thione sulphur. The magnetic moment of Co(II) complexes has been found between 4.96-4.72 B. M. The value is slightly higher than the μ_s value corresponding to three unpaired electrons (3.872 B.M). The increase in value may be attributed to orbital contribution from $^4T_{1g}$ ground state cubic term. The appearance of four bands in their electronic spectra is indicative of tetragonally distorted octahedral geometry of Co(II) complexes. The magnetic moment (3.20-3.30 B. M.) and appearance of 4 bands in the electronic spectra of Ni(II) complexes confirms the distorted octahedral geometry of the complexes. The magnetic moment of Cu(II) complexes has been determined to be (1.95-2.20 B. M.) which shows that Cu(II) complexes are magnetically dilute complexes. The appearance of three bands in their electronic spectra confirms John - Tellor distortion in octahedral symmetry of Cu(II) complexes. The various crystal field parameters exhibiting tetragonal distortion in the octahedral symmetry have also been derived. The positive value of D_t predicts tetragonal elongation in O_h symmetry.

Keywords: Tetragonally distorted, Tetragonal elongation, O_h symmetry

INTRODUCTION

The thiosemicarbazide and derivatives

has broad spectrum of applications in various fields. In biological field they may be used as fungicides, insecticides, algacides, plant growth regulators,



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enzymatic aldolisation catalyst, antiviral antibiotic agents etc.¹⁻⁶. One of the major development in the field of bio-organic chemistry is the finding that tin compounds of thiosemicarbazides can play an important role in anticortigenesis as Tondon *et al.*,⁷ have recently screen the di-n-butyltin complexes of Schiff base derived from S-substituted dithiocarbazate and fluoroaniline for their antitumour activity in lymphocyte leukaemia tumour system. The Schiff's base of S-methylthiocarbazate and its transition metal complexes have been studied for their cytotoxic action on potent antifungal activities⁸⁻⁹. Terephthalic acid bis (4-phenylthiosemicarbazone) has been found tetradentate chelating agent coordinating through the thiol-S and azomethine-N. Semicarbazones and thiosemicarbazones are important class of organic compounds, which have remarkable biological properties¹⁰⁻¹². Due to their pharmaceutical properties and chelating nature, their complexes have extensively been studied during the recent years¹³⁻¹⁶.

These significances of thiosemicarbazone complexes, have steered us to undertake the present study that involves the synthesis and characterisation of some complexes of Co(II), Ni(II) and Cu(II) with thiosemicarbazone of 3-hydroxy-4-methoxybenzaldehyde and their antibacterial evaluation.

MATERIAL AND METHODS

All the reagents used were of AnalR. Grade.

3-Hydroxy-4-methoxybenzaldehyde was procured from Aldrich & Co. while thiosemicarbazidehydrochloride was procured from BDH.

A Schiff's base ligand, 3-hydroxy-4-methoxybenzaldehydethiosemicarbazone was prepared by the condensation of 3-hydroxy-4-methoxybenzaldehyde and thiosemicarbazide and was used for complexation with Co(II), Ni(II) and Cu(II). The metal salts ($MX_2 \cdot 6H_2O$, where $X = Cl^-$, NO_3^- , CH_3COO^-) and ligand were taken in 1:2 molar ratio in ethanolic medium and solution was refluxed for 3 to 4 hours. On cooling the solution, coloured precipitate was obtained, which was filtered and washed with alcohol and dried in desiccator on anhydrous $CaCl_2$. The complexes were micro analysed for C, H, N and S and their m.p. was noted down.

The molar conductivity of complexes was determined in DMF solution of 10^{-3} M concentration on conductivity meter, C.G. 857 Schoolgrate GmbH having Pt-electrode. The magnetic susceptibility of complexes has been determined on Guoy balance at room temperature. The I.R. spectra of complexes were recorded Shimadzu FTIR-8400S spectrophotometer using KBr disc method. Electronic spectra of complexes were recorded on Shimadzu UV-160 spectrophotometer in DMF solution.

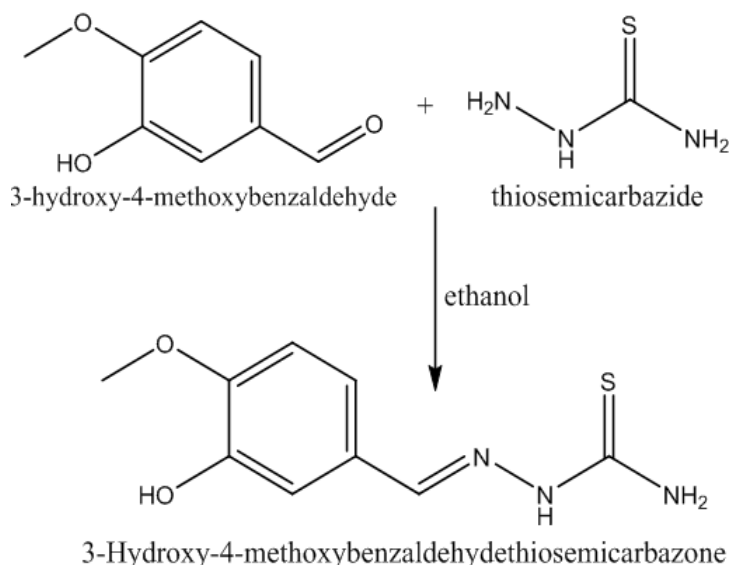


Table 1: Physical and Micro analytical Data of Ligand and Complexes

Compounds	Elemental analysis (%) : Calcd. (Found)						% yield	m.p. (°C)	Molar conductivity (λ), (ohms ⁻¹ cm ² mol ⁻¹)	Magnetic moment (μ _{eff}) (B.M.)
	Metal	C	H	N	S	Cl				
1. Ligand(HMBTS): [C ₉ H ₁₁ N ₃ O ₂ S]	–	48 (48.35)	4.89 (4.7)	18.67 (18.85)	14.23 (14.18)	–	85	312	11.5	4.7
2. [Co(HMBTS) ₂ Cl ₂]	10.16 (9.86)	37.25 (37.78)	3.8 (3.71)	14.48 (14.42)	10.16 (9.86)	12.24 (12.11)	78	314	15	4.69
3. [Co(HMBTS) ₂ (NO ₃) ₂]	9.31 (9.19)	34.13 (34.35)	3.48 (3.42)	17.7 (17.61)	10.11 (10.06)	–	83	315	12.35	4.72
4. [Co(HMBTS) ₂ (CH ₃ COO) ₂]	9.4 (9.32)	42.11 (42.34)	4.47 (4.35)	13.4 (13.35)	10.21 (10.11)	–	74	318	17	3.25
5. [Ni(HMBTS) ₂ Cl ₂]	10.11 (10.25)	37.27 (37.39)	3.8 (3.39)	14.49 (17.63)	11.04 (10.00)	12.25	75	317	18	3.2
6. [Ni(HMBTS) ₂ (NO ₃) ₂]	9.26 (9.14)	34.14 (34.32)	3.48 (3.39)	17.7 (17.63)	10.12	–	77	316	14	3.3
7. Ni(HMBTS) ₂ (CH ₃ COO) ₂]	9.35 (9.22)	42.13 (42.36)	4.47 (04.40)	13.4 (13.34)	10.21 (10.12)	–	81	330	15.32	1.95
8. [Cu(HMBTS) ₂ Cl ₂]	10.86 (10.77)	36.95 (37.24)	3.76 (3.71)	14.37 (14.30)	10.95 (10.88)	12.15 (12.08)	86	329	15.5	2.04
9. [Cu(HMBTS) ₂ (NO ₃) ₂]	09.96 (9.87)	33.90 (34.12)	3.45 (3.33)	17.56 (17.48)	10.13 (9.92)	–	83	332	15.48	2
10. [Cu(HMBTS) ₂ (CH ₃ COO) ₂]	10.06 (9.96)	41.8 (41.92)	4.43 (4.36)	13.3 (13.18)	10.13 (10.02)	–	85	312	11.5	4.7

RESULT AND DISCUSSION

The percentage composition of the ligand and complexes has been given in Table 1. On the basis of their molar conductivity and percentage composition the general formula of (ML₂X₂) has been assigned for the complexes. Where, L = 3-Hydroxy-4-methoxybenzaldehyde thiosemicarbazone X = Cl⁻, NO₃⁻ and CH₃COO⁻

The low value of molar conductivity of the complexes shows their non-electrolytic nature.

FTIR SPECTR

The sharp band appearing at 3520 cm⁻¹ is assigned of ν_{O-H} to phenolic group¹⁷⁻²¹ in the spectra to free ligand. This band does not undergo any change in the spectra of complexes, which shows its non-participation in coordination. The sharp band appearing at 1640 cm⁻¹ in the spectra of the free ligand and is assigned to ν_{CH=N}, which undergoes red shift and appears at 1615-1610 cm⁻¹ in the I.R. spectra of complexes, which is

indicative of co-ordination through azomethine nitrogen of the ligand²²⁻²³. A doublet observed at 1270 cm⁻¹ and 1260 cm⁻¹ is fairly assigned to ν_{CH₃O} group of the ligand^{24,25}. These bands remain intact in I.R. spectra of complexes. A sharp band appearing at 1200 cm⁻¹ in the I.R. spectra of free ligand is assigned to ν_{C=S}²⁶⁻³⁰. This band gets shifted to 1170-1160 cm⁻¹ in the I.R. spectra of complexes confirming the coordination through thione sulphur of the ligand. The band appearing at 3470, 3290 and 1360 cm⁻¹ due to ν_{NH₂}(assy.), ν_{NH₂}(Symm.) and ν_{NH}³¹⁻³⁴ respectively in the I.R. spectra of the free ligand do not show appreciable change in their frequency in complexes. Thus it is obvious that these groups are not involved in coordination. The appearance of new bands at 1460–1445 cm⁻¹, 1320–1310 cm⁻¹ and 1000–900 cm⁻¹ in the I.R. spectra of complexes number 3, 6 and 9 shows the presence of monodentately coordinated NO₃⁻ in these complexes³⁵⁻³⁸. The new bands appearing at 1630–1620 cm⁻¹ in the spectra of complexes numbers 4,7 and 10 clearly indicates the monodentately coordination of CH₃COO⁻ ion to the metal ions in these complexes³⁹⁻⁴¹. The bands

appearing in the far infrared region at 500–490, 420–400 and 370–365 cm^{-1} are assigned to $\nu_{\text{M-N}}$, $\nu_{\text{M-S}}$ and $\nu_{\text{M-Cl}}$ stretching vibrations respectively. Thus the ligand behaves as neutral bidentate coordinating through thione sulphur and azomethine nitrogen forming a very stable five membered ring.

Magnetic Moment and Electronic Spectra

The magnetic moment of Co(II) complexes has been found to be 4.69 – 4.72 B.M., which is greater than μ_{S} corresponding to three unpaired electrons ($t^5 e^2 e_g$) in high spin octahedral complexes of Co(II). This may be attributed to the lowering of symmetry from cubic one due to presence of different axial ligands. Thus μ_{eff} values predict

distorted octahedral symmetry around Co(II) in these complexes.⁴²⁻⁴⁵ In perfect octahedral symmetry of Co(II) complexes three bands are expected to appear in their electronic spectra due to three spin allowed transitions i.e., ${}^4T_{1g} \rightarrow {}^4T_{2g}$, ${}^4T_{1g} \rightarrow {}^4A_{2g}$ and ${}^4T_{1g} \rightarrow {}^4T_{2g}(\text{P})$. But here in the present case complexes display four bands which show the further splitting of, ${}^4T_{1g}(\text{F})$, ${}^4T_{2g}$ and ${}^4T_{1g}(\text{P})$ ⁴⁶. The band have been given in Table-2. The first three bands assigned to the transitions as $\nu_2 = {}^4A_{2g} \rightarrow {}^4E_g(\text{b})$, $\nu_3 = {}^4A_{2g} \rightarrow {}^4B_{2g}$ and $\nu_4 = {}^4A_{2g} \rightarrow {}^4B_{1g}$. The fourth band is broad and is not well resolved, hence it is assumed to consist of two transitions i.e., ${}^4A_{2g} \rightarrow {}^4E_g(\text{c})$ [${}^4T_{1g}(\text{P})$] and ${}^4A_{2g} \rightarrow {}^4A_{2g}(\text{c})$ [${}^4T_{1g}(\text{P})$]. The bands corresponding to $\nu_1 = {}^4A_{2g} \rightarrow {}^4E_g(\text{a})$ is not observed in the spectra.

Table 2 (cm^{-1})

Complexes	Band-1	Band-2	Band-3	Band-4
[Co(HMBTS) ₂ Cl ₂]	7,840	10,200	19,980	20,800
[Co(HMBTS) ₂ (NO ₃) ₂]	8,200	8,560	16,280	20,500
[Co(HMBTS) ₂ (CH ₃ COO) ₂]	7,280	10,230	19,490	21,000

On the basis of energy levels of different crystal field terms the various crystal field parameters and ν_1 have been derived and the values have been displayed in Table-3.

The values are in good agreement with that of tetragonally distorted octahedral complexes of Co(II)^{47, 48}.

The magnetic moment of Ni(II) complexes has been found 3.20–3.30 B.M., which are in good agreement with the values reported for six coordinated Ni(II) complexes^{49,50}. The electronic spectra of Ni(II) complexes display four bands which have been given in Table-4.

Table 3 (cm^{-1})

Complexes	$D_{q(xy)}$	$D_{q(z)}$	D_s	D_t	ν_1
1. [Co(HMBTS) ₂ Cl ₂]	978	1278.3	-2,335.4	-171.60	3,368
2. [Co(HMBTS) ₂ (NO ₃) ₂]	770	818	-2,110.0	-27.60	1,974
3. [Co(HMBTS) ₂ (CH ₃ COO) ₂]	826	1201.5	-2,289	-214.60	2,297

Table 4 (cm^{-1})

Complexes	ν_1	ν_2	ν_3	ν_4
1. [Ni(HMBTS) ₂ Cl ₂]	8,600	17,750	15,200	19,400
2. [Ni(HMBTS) ₂ (NO ₃) ₂]	8,500	14,200	15,800	19,600
3. [Ni(HMBTS) ₂ (CH ₃ COO) ₂]	8,750	14,600	15,400	19,350

The assignment of these bands with their energy are given below

- (i) $\nu_1 = {}^3B_{1g} \rightarrow {}^3E_g(\text{a})$; $\Delta E = 10D_q - 35/4 D_t$
 (ii) $\nu_2 = {}^3B_{1g} \rightarrow {}^3E_{2g}$; $\Delta E = 10D_q$.

- (iii) $v_3 = {}^3B_{1g} \rightarrow {}^3A_{2g}(a)$; $\Delta E = 18D_q - 4D_s - 5D_t$ measure of $10D_q$ in plane, i.e., $10D_{qxy}$. The various
 (iv) $v_4 = {}^3B_{1g} \rightarrow {}^3E_g(b)$; $\Delta E = 18D_q + 2D_s - 25/4 5D_t$ crystal field parameters have been derived from the
 energy associated with different transitions and the
 values have been displayed in Table-5.

v_2 is free from D_t and D_s and thus it is a

Table 5(cm^{-1})

Complexes	$D_{q(xy)}$	$D_{q(z)}$	D_s	D_t
1. $[\text{Ni}(\text{HMBTS})_2\text{Cl}_2]$	1475	245	846.4	702.8
2. $[\text{Ni}(\text{HMBTS})_2(\text{NO}_3)_2]$	1420	280	769	651.4
3. $[\text{Ni}(\text{HMBTS})_2(\text{CH}_3\text{COO})_2]$	1460	290	797.6	668.57

The values support a tetragonal distortion in the octahedral symmetry of Ni(II) complexes.⁵¹⁻⁵² From the value of D_t and D_s , it is clear that the distortion capacity is maximum for Cl^- and minimum for NO_3^- ligand.

Cu(II) complexes have shown magnetic moment 1.95–2.04 B.M., which corresponds the presence of one unpaired electron indicating mononuclear nature of complexes with dilute paramagnetism⁵³⁻⁵⁶.

These complexes display three bands in their electronic spectra, which has been given in Table-6.

Table 6 (cm^{-1})

Complexes	v_1	v_2	v_3
1. $[\text{Cu}(\text{HMBTS})_2\text{Cl}_2]$	12,100	14,100	17,100
2. $[\text{Cu}(\text{HMBTS})_2(\text{NO}_3)_2]$	9,250	11,250	13,250
3. $[\text{Cu}(\text{HMBTS})_2(\text{CH}_3\text{COO})_2]$	11,000	13,400	15,900

These bands has been assigned to the following spin allowed transition with their energy⁵⁷.

$$v_1 = {}^2B_{1g} \rightarrow {}^2A_{1g} = -6D_q + 2D_s + 6D_t + 6D_q + 2D_s - D_t = 4D_s + 5D_t$$

$$v_2 = {}^2B_{1g} \rightarrow {}^2B_{2g} = 4D_q - 2D_s + D_t + 6D_q + 2D_s - D_t = 10D_q$$

$$v_3 = {}^2B_{1g} \rightarrow {}^2E_g = 4D_q + D_s - 4D_t + 6D_q + 2D_s - D_t = 10D_q + 3D_s - 5D_t$$

The values of different parameter have been derived using above equations and shown in Table-7.

Table 7 (cm^{-1})

Complexes	$D_{q(xy)}$	$D_{q(z)}$	D_s	D_t
1. $[\text{Cu}(\text{HMBTS})_2\text{Cl}_2]$	1410	1503	3775	1665
2. $[\text{Cu}(\text{HMBTS})_2(\text{NO}_3)_2]$	1125	1128	2812.5	1287.5
3. $[\text{Cu}(\text{HMBTS})_2(\text{CH}_3\text{COO})_2]$	1340	1328.75	3375	1525.00

The values are in good agreement with those reported for tetragonally distorted Cu(II) complexes⁵⁸⁻⁶¹.

Bioactivity measurements

The ligands as well as all the complexes were screened for the *in vitro* antibacterial activities against *Escherichia Coli*, *Citrobacter gillenii* using the agar disk diffusion method⁶². The antibiotic, Chloramphenicol has been taken as standard for comparison. Autoclave Nutrient agar medium was poured into sterile peri-dish after dipping the test compound in DMSO solution. The width of the growth inhibition zone around the disc was measured after 24 h incubation at 35°C temperature. Since DMSO was used as solvent, it was also screened against whole organisms and no activity was found. The antibacterial data have been given in Table-8.

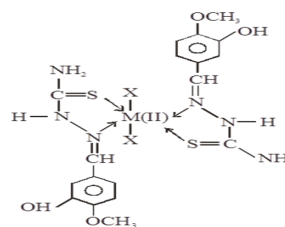
It is obvious from the data that all the complexes exhibit enhanced biological activity than the ligand, but lesser activity than the standard at whole the concentration. It is also clear that at 100 $\mu\text{g/ml}$ concentration the inhibition is very low compare to higher concentration. The complex of Cu(II) are found more active than other complexes at all the concentration. This may be due to stronger biological activity of Cu (II) than Co(II) and Ni(II). The enhancement of biological activity of the ligand after complexation may be attributed by chelate formation which fascinates the complex across the cell membrane.⁶³⁻⁶⁵

Table 8 : Antibacterial activity data of ligand and complexes Inhibition Zone in mm

S.No.	Compounds	<i>E-coli</i> Concentration		<i>Citrobactor gillenii</i> Concentration			
		500 µg/mL	250 µg/mL	100 µg/ mL	500 µg/ mL	250 µg/ mL	100 µg/ mL
1	3-hydroxy-4-methoxybenzaldehyde thiosemicarbazone(HMBTS)	7	6	4	8	8	7
2	[Co(HMBTS) ₂ Cl ₂]	14	14	8	13	12	8
3	[Co(HMBTS) ₂ (NO ₃) ₂]	15	14	9	14	12	8
4	[Co(HMBTS) ₂ (CH ₃ COO) ₂]	13	12	8	14	13	9
5	[Ni(HMBTS) ₂ Cl ₂]	15	13	10	14	11	8
6	[Ni(HMBTS) ₂ (NO ₃) ₂]	14	13	9	15	13	9
7	Ni(HMBTS) ₂ (CH ₃ COO) ₂	13	13	10	13	13	9
8	[Cu(HMBTS) ₂ Cl ₂]	18	17	11	16	15	10
9	[Cu(HMBTS) ₂ (NO ₃) ₂]	19	17	10	17	15	10
10	[Cu(HMBTS) ₂ (CH ₃ COO) ₂]	16	15	10	16	14	9
11	Standard (Chloramphenicol)	40	39	33	35	34	30

CONCLUSION

The ligand 3-Hydroxy-4-methoxybenzaldehyde thiosemicarbazone acts as neutral bidentate ligand coordinating through thione sulphur and azomethine nitrogen forming five membered ring with the metal ions. Due to the presence of different axial ligands all these complexes are appreciably tetragonally distorted. It is also revealed that the distortion capacity of chloride is maximum while that of nitrate is minimum, which may be attribute to the greater coordinating capacity of NO₃⁻ in respect of Cl⁻ and CH₃COO⁻. Cl⁻ having weakest coordinating capability remain at lower distance from metal ions along z-axis and hence their is greater tetragonal distortion in octahedral symmetry of complexes. The tentative structure may be given as below.



Bioactivity measurement reveals that all the complexes are biologically more active against both *E-coli* and *c-gillenii* than the free ligand but less active than standard Chloramphenicol.

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