

Physicochemical and Biological Studies on Metal (II) Complexes with Methoxy Benzofuran Bromophenylthiosemicarbazide Derivative

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Abstract:

The complexes of the type $MLCl_2$, where $M = Co(II), Cu(II), Ni(II), Zn(II), Cd(II)$ and $Hg(II)$ and L is the thiosemicarbazide ligands derived from reaction between 3-methoxybenzofuran-2-carboxyhydrazide and p-bromophenylisothiocyanate (MBCBrPT). All the complexes were characterized on the bases of elemental analysis, conductance, magnetic susceptibility measurements, UV-Vis, IR, ^1H NMR, ESR spectra studies and X-ray data studies. Thiosemicarbazide ligands behave as bidentate by coordinating through the oxygen of the carbonyl group and the nitrogen of the hydrazide residue. Based on the results, we have proposed the probable structures for all the metal complexes. Both the ligands and their complexes have been screened for their fungicidal and bactericidal activities

Keywords: methoxybenzofuran p-bromothiosemicarbazides, Metal Complexes, Spectral Studies and antimicrobial activities.

1. Introduction

Thiosemicarbazides and thiosemicarbazones have special attention due to their activity against protozoa¹, influenza², small-pox³, malaria, cancer⁴ and tuberculosis. As a ligand they provide three potential donor sites viz, O, N and S and form complexes with various metal ions. The metal complexes with thioderivatives of hydrazine have occupied a very important place in the future development and progress of coordinating chemistry. A study of complexes with thioderivatives of hydrazine is therefore of particular interest. Thiosemicarbazones and their 3d-metal complexes have been found to exhibit fungicidal, bactericidal, antiviral and antitumor activity. Owing to the wide range of microbial properties^{5,6} of their thiosemicarbazides and thiosemicarbazones and their ability to form chelates with metal ions, in the present study, we report the synthesis and characterization of $Cu(II)$, $Co(II)$, $Ni(II)$, $Zn(II)$, $Cd(II)$, $Hg(II)$, $Mn(II)$ and $Fe(III)$ metal complexes with the thiosemicarbazide ligand derived from reaction between 3-methoxybenzofuran-2-carboxyhydrazide and p-bromophenylisothiocyanate. All the complexes have been characterized by Elemental analysis, Conductance, Magnetic Susceptibility measurements, UV-Vis, IR, ^1H NMR, ESR spectral studies and X-ray data studies.

2. Experimental

All the chemicals used were of Analytical Grade. The compound benzophthofuran-2-carboxyhydrazide was prepared by the literature method⁷. The metal and chloride contents are determined as per Vogel's procedure⁸. The nitrogen content was estimated micro-analytically.

Preparation of 3-methoxybenzofuran-2-carboxy-[4'-bromophenyl] thiosemicarbazide [MBCBrPT]

The p-bromophenylisothiocyanate (0.5 mole) in alcohol (10 cm³) was added to an ethanolic (20 cm³) solution of 3-methoxybenzofuran-2-carboxyhydrazide (1.7 g, 0.5 mole). The reaction mixture was boiled under reflux water bath for about 3-4 hours. The solid thiosemicarbazide ligand starts separating out after few minutes. The reaction mixture was cooled room temperature; product was filtered out and washed successively with alcohol. The compound was recrystallized from alcohol and dried in vacuum over fused CaCl₂.

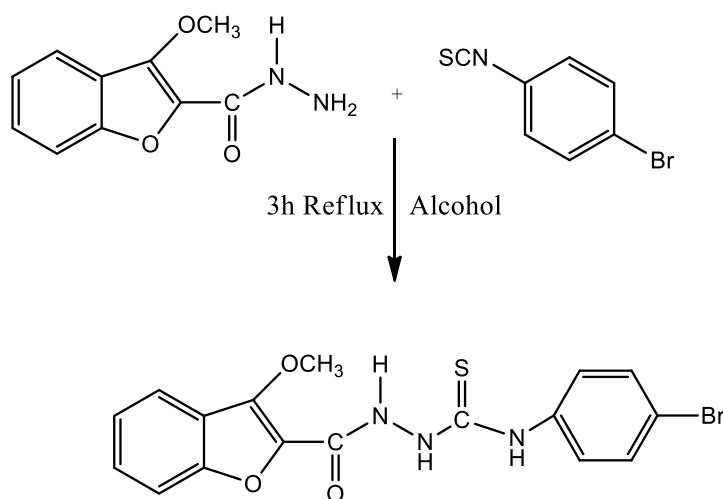
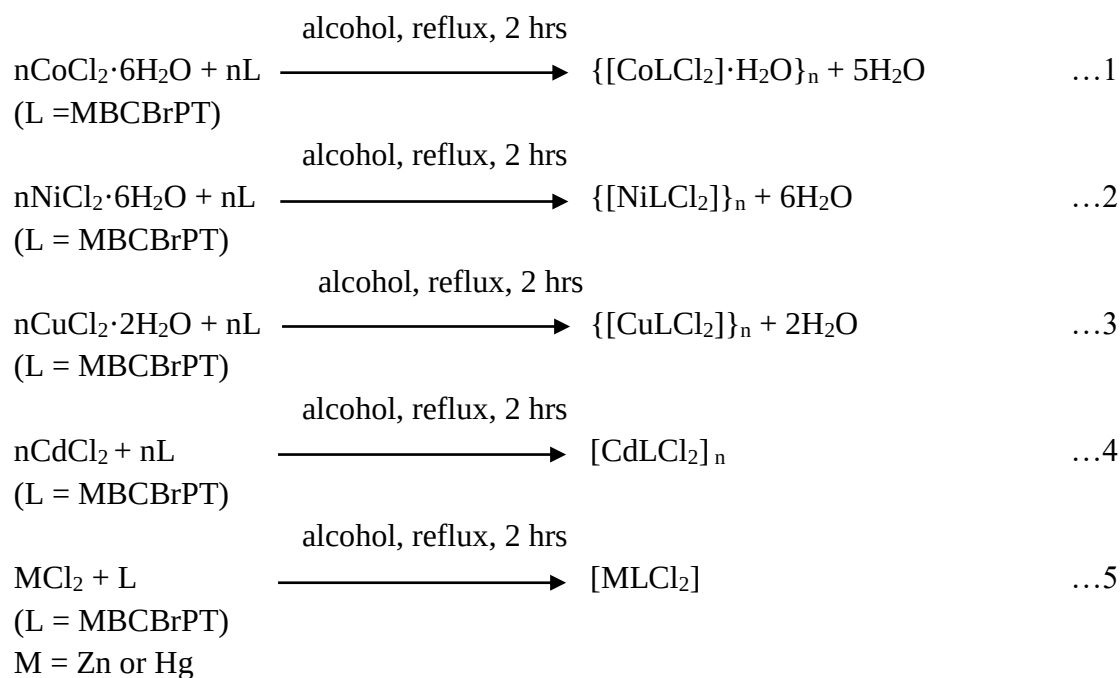


Figure-1 ligand

[Mol. formula – C₁₇H₁₄O₃N₃SBr, M.P. = 195⁰C, yield 85% and M.W. 420.28]

3. Preparation of Complexes

Metal complexes were prepared by adding the aqueous solution of metal(II) chlorides(0.1mole, 20 cm³) to thiosemicarbazide ligand (1.55 g MBCPT; 1.73 g MBCBrPT, 0.1mole) in alcohol(50 cm³) with vigorous stirring. The complexes were not separated immediately, the reaction mixture was boiled under reflux on a water bath for about 2 hours, during which complexes started separating out. The reaction solution was concentrated and cooled to room temperature. The crystalline light colored complexes were filtered, washed with water and alcohol to remove the un-reacted salts and ligands. All the complexes were dried in open air and kept in vacuum desiccator. The formation of the complexes may be represented by the following equations



4. Physical measurements

All the complexes were analyzed for their metal content, following the standard procedures⁸. Sulphur and chloride contents were determined as BaSO₄ and AgCl₂, respectively. The magnetic susceptibility measurements were made at room temperature on a Gouy balance using Hg[Co(NCS)₄] as the calibrate. Electronic spectra of the Cu(II), Co(II) and Ni(II) complexes in DMF (10⁻³ M) solution were recorded using a Hitachi 150-20 model spectrophotometer in the range of 200-1100 nm. IR spectra of the ligands and their complexes were recorded in KBr pallets on Perkin Elmer-783 model IR spectrometer in the range of 4000-350 cm⁻¹ and Impact 410 Nicolet FT-IR spectrometer in the range of 4000-250 cm⁻¹. The proton magnetic resonance spectra of ligands and few complexes were recorded on a Brucker 300 MHz at IISc Bangalore and Bracker A.C. 300 F at USA, NMR spectrometer using TMS as an internal standard and DMSO-d₆ were used as solvents. The electron spin resonance spectra of Cu(II) complexes in polycrystalline state (powder spectra) were recorded on Varian E-4X-band ESR spectrometer using tetracyanoethylene (TCNE) free radical as 'g' marker (g=2.0036) at room temperature. The X-ray spectra were recorded on Phillips PW 3710 diffractometer attached to a digitized computer along with graphical assembly using CuK α radiation source. The X-ray tube was operated at 25KV/20mA. The sample was scanned in the 2 θ range from 0-80°C at a scanning speed of 2 θ /min.

The antimicrobial activities of the compounds synthesized in the present investigation were screened for their antibacterial and antifungal activities by agar cup plate technique⁹. These bacterial species namely Escherichia coli, Pseudomonas and Bacillus and three fungal species Aspergillus Niger, Aspergillus fumigatus and Aspergillus flavons procured from the Department of Microbiology, Gulbarga University, Gulbarga were used in the present study. DMF was used as the solvent and it has been well established as an inert solvent with negligible antimicrobial activity. The experiments were conducted in triplicate and the average activity is reported

5. Results and Discussions

Analytical data for the complexes indicate 1:1 stoichiometry for all the complexes table-1. All the complexes possess high melting points and are stable towards air and are partially or insoluble in common organic solvents and soluble in DMF, DMSO and Pyridine. The molar conductance of the complexes fall in the range of 9.948- 19.826 $\Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ in DMF (10^{-3}M) solution. The values are too low to account for any electrolytic behaviors of the complexes¹⁰.

The observed magnetic moment values for Co[MBCBrPT] complexes is 4.52 B.M. respectively, have been used as a criterion to determine the type of geometry around the metal ions, these values suggests an octahedral geometry for Co(II) complexes¹¹. The observed magnetic moment values for Mn[MBCBrPT] complexes is 5.69 B.M. respectively, have been used as a criterion to determine the type of geometry around the metal ions. The observed magnetic moment values for Fe[MBCBrPT] complexes is 5.88 B.M. respectively, have been used as a criterion to determine the type of geometry around the metal ions. The magnetic moment values is Ni(II) complexes 3.29 B.M. Ni[MBCBrPT] ligand respectively, suggests the hexa-coordinated Ni(II) ions¹². The effective magnetic value for Cu[MBCBrPT] complexes is 2.21 B.M. respectively suggests, the distorted octahedral geometry.

6. Electronic Spectra

The electronic spectra of Co(II) complexes show two bands at 16611 and 20161 cm^{-1} for [MBCBrPT] respectively, these bands are assigned to $^4\text{T}_{1g}(\text{F}) \rightarrow ^3\text{A}_{2g}(\text{F})(\nu_2)$ and $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})(\nu_3)$ transitions, respectively, in an octahedral environment^{13,14}. The band ν_1 could not be observed due to the limited range of the instrument; however, ν_1 would be calculated using band-fitting procedures¹⁵. The octahedral geometry¹⁶ is further supported by the values of ligand field parameters like, Dq, B', β , $\beta\%$ and LFSE. All these values are given in the table-2. The reduction in Racah parameter value from the free ion value (971) suggests measure of covalent character of M-L bond.

The hexa-coordinated light green colored Ni[MBCBrPT] complexes exhibit two bands at 17006 and 27027 cm^{-1} respectively assignable to $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})(\nu_2)$ and $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{P})(\nu_3)$ transitions, respectively, in view of their octahedral geometry¹³. This is further supported by ligand field parameters like Dq, B', β , $\beta\%$, ratio $(\nu_2) / (\nu_1)$ and LFSE values shown in table-2.

The coordinated light greasy colored Mn[MBCBrPT] complexes exhibit two bands at 23394 and 28169 cm^{-1} respectively assignable to $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})(\nu_2)$ and $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{P})(\nu_3)$ transitions, respectively, in view of their polymeric octahedral geometry.

The coordinated light rust colored Fe[MBCBrPT] complexes exhibit two bands at 20876 and 25125 cm^{-1} respectively assignable to $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})(\nu_2)$ and $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{P})(\nu_3)$ transitions, respectively, in view of their monomeric octahedral geometry

The Cu(II) complexes shows broad asymmetric band in the region 15384-17605 cm^{-1} . The broadness of the band may be due to dynamic Jahn-Teller distortion¹⁷. These observations suggest that complexes have distorted octahedral structures.

7. ^1H NMR spectra

The ^1H NMR spectrum of [MBCBrPT] ligands and their Cd(II) and Hg(II) complexes in DMSO- d_6 solvents were recorded. The three signals at, $\delta(10.11, 10.23)$, $\delta(9.81, 9.89)$ and $\delta(9.75, 9.80)$ ppm, due to ^1NH , ^2NH and ^4NH protons of amide, hydrazine and thioamide functions respectively. The signal appeared at $\delta(3.40)$ and $\delta(3.53)$ due to the methoxy proton present in the benzofuran ring. Nine aromatic proton have resonated in the region $\delta(7.02-7.97)$ (m, 9H) and Eight aromatic proton present in the region $\delta(7.13-7.87)$ (m, 8H) as a multiplet respectively.

The signals due to ^2NH proton are shifted down field in the spectra of Hg(II) complexes and the signals due to ^1NH proton shows a small down field shift thereby indicating the coordination of ligands through the oxygen of CONH and nitrogen of ^2NH groups to the metal ions. The methoxy proton and aromatic region are disturbing its ligands signals it indicates the coordination of ligands takes place in the metals.

Infrared spectra

The thiosemicarbazide ligand [MBCBrPT] exhibits the three bands at 3343, 3294, 3127 cm^{-1} assigned to $\nu(^4\text{NH})$, $\nu(^2\text{NH})$ and $\nu(^1\text{NH})$ respectively, in view of the earlier reports^{18,19}. In the spectra of the complexes the bands due to $\nu(^4\text{NH})$ shifts to higher wave number side by about 10-30 cm^{-1} or it remains unaltered indicating non-involvement of nitrogen of (^4NH) group in coordination with metal ions. The band due to $\nu(^2\text{NH})$ shifts to lower wave number side by about 21-35 cm^{-1} in all the complexes and becomes weak in the complexes suggesting the coordination of the nitrogen of (^2NH) group. The bands observed in the region 3268-3257 cm^{-1} are remain practically unaltered or shift slightly to higher wave number side indicating no coordination.

The weak bands observed in the regions 2775-2840 cm^{-1} are assigned to stretching vibrations of intra-molecular hydrogen bonding between -CO and ^2NH group²⁰. The absence of any band above 3500 cm^{-1} due to $\nu(\text{OH})$ stretch and 2650-2450 cm^{-1} due to $\nu(\text{SH})$ stretch suggests that ligand exists in thioketo form.

The strong band observed²¹ at 1659 cm^{-1} in free ligands are assigned to $\nu(\text{CO})$ stretching vibrations. These bands shift to lower wave number side by about 25-52 cm^{-1} in all the metal complexes. This suggests the coordination of oxygen with metal ions. The positive shift of $\nu(\text{N-N})$ stretch observed at 971 cm^{-1} in free ligands by 10-15 cm^{-1} in the complexes, thereby, showing the coordination of the one of the nitrogen atom of the hydrazinic moiety in bonding²².

The thioketo $\nu(\text{C=S})$ band observed at 740 cm^{-1} shows no shift in the metal complexes compared with the free ligands, this shows sulphur atom of (C=S) group has not been taken part in the coordination. The thio-amide²³ bands observed at 1525; 1332; 1064 and 715 cm^{-1} due to amide I, II, III and IV respectively, remain unaltered or do not show considerable change in the complexes suggesting the non-involvement of (C=S) group in bonding with metal ions.

In the far infrared spectra of the complexes the bands observed in the region $582\text{--}495\text{ cm}^{-1}$ can be assigned to $\nu(\text{M-O})$ stretching vibrations and bands in the region $471\text{--}382\text{ cm}^{-1}$ to $\nu(\text{M-N})$ stretching vibrations in all the complexes²⁴.

In the case of polymeric complexes $\nu(\text{M-Cl})$ stretch terminal and $\nu(\text{M-Cl})$ stretch bridging are assigned in the region $349\text{--}321\text{ cm}^{-1}$ and $316\text{--}282\text{ cm}^{-1}$ respectively, in view of previous reports²⁵, in Co(II), Cu(II), Ni(II) and Cd(II) complexes. In Hg(II) and Zn(II) complexes $\nu(\text{M-Cl})$ stretch is assigned in the region $334\text{--}316\text{ cm}^{-1}$ in view of their monomeric /diameric structures. All assignments in table-3.

ESR spectra

The ESR spectrum of Cu(II) complex of ligand [MBCBrPT] in solid polycrystalline state have been scanned at room temperature. These Cu(II) complexes showed medium broad signals with of $g_{\parallel} = 2.3066$ and $g_{\perp} = 2.0098$ respectively. The g_{av} values of the complexes have been calculated and shown in table-4. The obtained g_{av} values for the Cu(II) complexes are 2.0858 for MBCBrPT ligands respectively. The 'g' values indicate that the free electron is predominantly in $d_{x^2-y^2}$ orbital of Cu(II). The 'G' values are less than 4 and it indicates anti ferromagnetic coupling interaction between the metal ions.

The sample Cu[MBCBrPT] show the spectra having asymmetric bands with two 'g' values, $g_{\parallel} > g_{\perp}$. The trend $g_{\parallel} > g_{\perp} > g_e$ (2.0036) observed for these complexes indicating that, the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital with the possibility of some mixing of d_{z^2} , because of low symmetry²⁶.

The bonding coefficients parameter K, $K_{\parallel}$, $K_{\perp}$, α^2 , β^2 and degree of covalency K_o^2 have been calculated which is the residential time of an unpaired electron on a Cu(II) ion, and the value of $g_{\parallel}$ (<2.3) confirm the covalent nature of the complexes^{27,28}.

8. Biological activity

The microbial activity results show that the compounds exhibit antimicrobial properties and it is important to note that the metal complexes exhibit more inhibitory effects than the parent ligands, the values are given in table-5. The increase in the antibacterial and antifungal activity of the metal complexes is due to the presence of metal ions in the compounds. The increased activity of the metal chelates can be explained on the bases of chelation theory²⁹. It is known that chelation tends to make the ligand act as more powerful and potent bactericidal agents, thus killing more of the bacteria than the ligand. It is observed that, in a complex, the positive charge of the metal is partially shared with donor atoms present in the ligand and there may be π -electron delocalization over the whole chelating³⁰. The complexes exhibited enhanced activities, which is due to the synergistic effect that increases the lipophilicity of the complexes. Chelation decreases the polarity of the metal ion which further leads to the enhancement of lipophilicity of the complex. Since the microorganism cell is surrounded by lipid membrane which favors the passage of lipid soluble materials, increased lipophilicities allows the penetration of the complex into, and through sites of the microorganisms. There are other factors which

also increase the activity, which are solubility, conductivity and bond length between the metal and ligand.

Antibacterial and antifungal screening data clearly to the following conclusion

1. The metal complexes are slightly more toxic than their parent ligand against tested microorganisms under identical experimental conditions.
2. The Microbial activity results indicate that the activity of Cu(II), Mn(II) and Zn(II) complexes show better activity than that of Co(II), Ni(II), Fe(II) and Cd(II) complexes.
3. The Microbial activity results clearly show that the inhibition of fungal growth increases with increasing the concentration of the complexes.

9. Conclusion

The ligand [MBCBrPT] acts as a neutral bidentate, coordinating through the amide-O and ^2NH nitrogen of the thiosemicarbazide function. All the complexes are isolated in solid state, possess 1:1 (M: L) stoichiometry.

On the basis elemental analysis, electronic spectra, magnetic susceptibility, IR, NMR and ESR spectral data, we suggest the following probable geometries to all the complexes.

1. For Cu(II), Co(II), Ni(II) Mn(II) and Cd(II) chloride bridged polymeric octahedral structure.
2. For Zn(II) and Hg(II) complexes monomeric/dimeric tetrahedral structures.
3. Monomeric octahedral structure to Fe(III) complexes.

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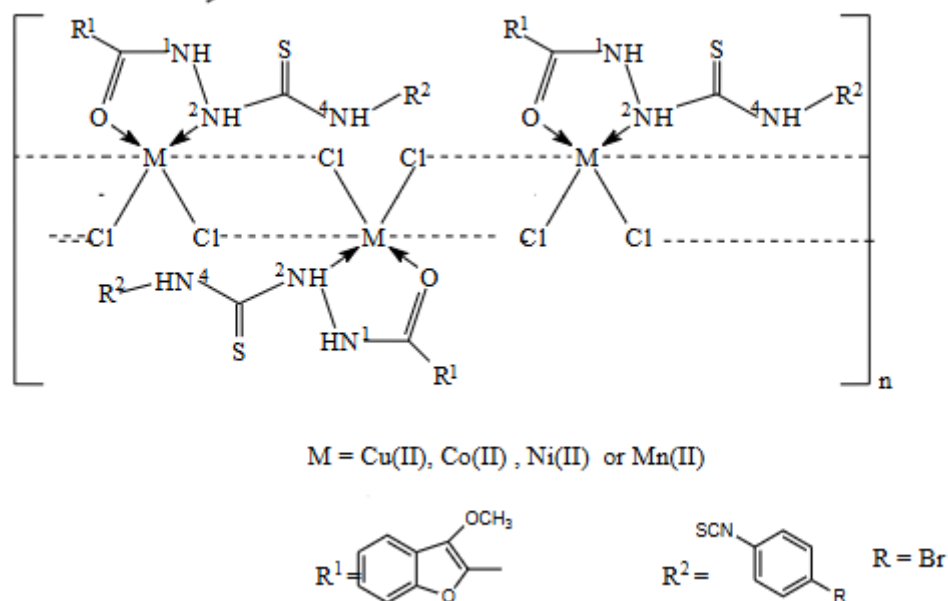


Figure-2 Suggested structures of the complexes

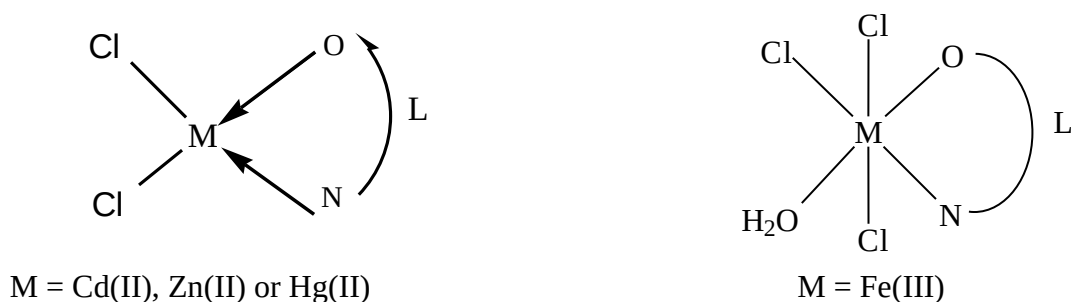


Figure-3 Suggested structures of the complexes

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Table-1

Physical, Analytical data, Magnetic Susceptibility and Molar Conductance data of MBCPT ligand and its complexes

Compound	Empirical formula/ Molecular formula	Mol . Wt	M. P °C	Yield %	Elemental analysis (%) Found / (Calculated)					μ_{eff} B. M	Molar conductance $\Lambda_{\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}}$
					M	C	H	N	Cl		
[MBCBrPT] [C ₁₇ H ₁₄ N ₃ O ₃ S ₁ Br] [410]	[Co(C ₁₇ H ₁₄ N ₃ O ₃ S ₁ Br)Cl ₂]	549.93	>300	75	10.345 (10.715)	37.450 (37.095)	2.780 (2.545)	7.247 (7.637)	13.078 (12.910)	4.52	14.503
	[Ni(C ₁₇ H ₁₄ N ₃ O ₃ S ₁ Br)Cl ₂]	549.71	>300	70	10.420 (10.680)	37.654 (37.110)	2.854 (2.546)	7.245 (7.640)	13.354 (12.915)	3.29	16.695
	[Cu(C ₁₇ H ₁₄ N ₃ O ₃ S ₁ Br)Cl ₂]	554.50	289	75	11.220 (11.451)	36.487 (36.789)	2.980 (2.524)	7.320 (7.574)	12.587 (12.804)	2.21	9.948
	[Zn(C ₁₇ H ₁₄ N ₃ O ₃ S ₁ Br)Cl ₂]	556.38	>300	70	11.458 (11.750)	36.254 (36.663)	2.780 (2.516)	7.220 (7.548)	12.560 (12.760)	--	15.473
	[Cd(C ₁₇ H ₁₄ N ₃ O ₃ S ₁ Br)Cl ₂]	603.41	>300	70	18.990 (18.629)	33.348 (33.807)	2.687 (2.320)	6.520 (6.960)	11.520 (11.766)	--	16.796
	[Hg(C ₁₇ H ₁₄ N ₃ O ₃ S ₁ Br)Cl ₂]	691.59	298	85	28.725 (28.989)	29.780 (29.482)	2.452 (2.023)	6.420 (6.072)	10.642 (10.266)	--	15.180
	[Mn(C ₁₇ H ₁₄ N ₃ O ₃ S ₁ Br)Cl ₂]	545.93	285	80	10.450 (10.061)	37.488 (37.637)	2.879 (2.564)	7.234 (7.693)	13.540 (13.005)	5.69	12.635

	[Fe(C ₁₇ H ₁₄ N ₃ O ₃ S ₁ Br)Cl ₃].H ₂ O	600.34	289	70	10.457 (10.211)	37.458 (37.350)	2.875 (2.560)	7.348 (7.680)	12.647 (12.983)	5.88	19.816
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Table-2

Electronic Spectral data and Ligand field parameter of the Co(II), Ni(II), Cu(II) Fe(III) and Mn(II) Complexes with Thiosemicarbazide in DMF (10⁻³M) solution.

Ligand	Complexes	Transition in cm ⁻¹		Dq cm ⁻¹	B ¹ cm ⁻¹	β	β%	v ₂ / v ₁	L.F.S.E k.cal
		v ₁ [*]	v ₂						
MBCBrPT	[Co(C ₁₇ H ₁₄ N ₃ O ₃ S ₁ Br)Cl ₂]	7748		887	903	0.9298	07.106	1.213	15.18
MBCBrPT	[Ni(C ₁₇ H ₁₄ N ₃ O ₃ S ₁ Br)Cl ₂]	16611		1083	1083	0.7399	26.057	1.589	37.13
MBCBrPT	[Cu(C ₁₇ H ₁₄ N ₃ O ₃ S ₁ Br)Cl ₂]	20161	--	1649	1649	--	--	--	28.26
MBCBrPT	[Fe(C ₁₇ H ₁₆ N ₃ O ₄ S ₁ Br)Cl ₃]	10830		--	--	--	--	--	--
MBCBrPT	[Mn(C ₁₇ H ₁₄ N ₃ O ₃ S ₁ Br)Cl ₂]	17006		--	--	--	--	--	--
		27027	--						
		15384	--						
		17605							
		16611							
		20876							
		25125	--						
		17006							
		23394							
		28169							
		32679							

* Calculated values.

Table-3
Infrared Spectra of the Thiosemicarbazide base of ligand [MBCBrPT] and its Complexes

Ligand / Complexes	$\nu^{4\text{NH}}$ sym streich	$\nu^{2\text{NH}}$ sym streich	$\nu^{1\text{NH}}$ sym streich	$\nu_{\text{N-N}}$	$\nu_{\text{C=O}}$	$\nu_{\text{M-O}}$	$\nu_{\text{(M-N)}}$	$\nu_{\text{(M-Cl)t}}$	$\nu_{\text{(M-Cl)b}}$	$\nu_{\text{(M-Cl)}}$
MBCBrPT	3343	3294	3127	971	1659	--	--	--	--	--
Cu	3343	3250	3140	1013	1613	496	471	330	298	--
Co	3347	3257	3129	1005	1608	495	442	321	291	--
Ni	3361	3261	3128	1005	1614	510	436	342	282	--
Zn	3359	3263	3137	1009	1604	538	466	--	--	316
Cd	3340	3263	3146	1010	1609	530	382	--	--	334
Hg	3346	3270	3151	1016	1607	552	448	--	--	321
Mn	3348	3268	3141	1005	1609	581	430	349	316	--
Fe	3338	3265	3148	1008	1613	582	459	--	--	321

Table-4
ESR spectral data of Cu(II) complexes.

Complex	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel} \times 10^{-4} (\text{cm}^{-1})$	$g_{\parallel} / A_{\parallel}$	α^2	G
MBCBrPT	2.3066	2.0098	2.0858	2.2120	208.37	8.025	0.007152

Bonding Coefficient Parameter for the Cu(II), Complexes with Thiosemicarbazide.

Complexes	$A_{\text{iso}} 1 \times 10^{-4} \text{cm}^{-1}$	$K_{\parallel}$	$K_{\perp}$	K	β^2	α	K_o^2
MBCBrPT	137.282	0.8406	0.8279	0.4646	2.4606	0.2312	0.3999

Table -5
Antibacterial and antifungal activity results of ligands and their metal complexes

Ligand/Complexes	Zone of inhibition (m.m)			
	Bacterial		Fungal	
	E.Coli	S.auriosus	A.niger	A.fumigatus
MBCBrPT	10	11	14	16
Cu(II)	12	10	08	10
Co(II)	11	10	09	12
Ni(II)	10	11	08	11
Zn(II)	14	12	10	16
Cd(II)	18	17	16	13
Mn(II)	13	12	12	10
Fe(III)	12	10	10	13
Cu(MBCBrPT)	12	10	12	13
Co(MBCBrPT)	13	11	13	11
Ni(MBCBrPT)	15	12	14	13
Zn(MBCBrPT)	14	15	12	14
Cd(MBCBrPT)	15	13	12	12
Mn(MBCBrPT)	17	14	13	12
Fe(MBCBrPT)	18	16	17	14
Standard				
Streptomycin	22	20	--	--
Nystatine	--	--	21	20
Control (DMF)	08	08	04	04