

Studies of Bivalent Metal Complexes of *p*-Chloro- & *p*-Methoxybenzylidene-4-phenylthiosemicarbazone

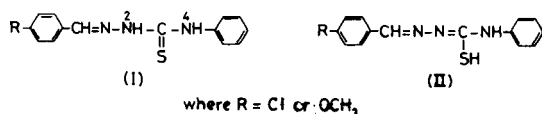
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Bivalent metal complexes of *p*-chloro- and *p*-methoxybenzylidene-4-phenylthiosemicarbazones (H_2CBPT and $H_2MBPT = H_2L$) have been prepared. The complexes prepared are of the types $M(HL)_2 \cdot nH_2O$ ($M = Co, Ni$ or Zn , $n = 0-2$), $M(HL)X \cdot nH_2O$ ($M = Cu$ or Hg ; $X = Cl$ or Ac and $n = 0-1$), $Cu(H_2CBPT)_2Ac_2$ and $Hg(H_2CBPT)Cl_2 \cdot 2H_2O$. The analytical and IR data show that H_2MBPT reacts in the thioenol form and acts in a monobasic bidentate manner, while H_2CBPT reacts in both thioketo and thioenol forms behaving in a neutral or in a monobasic bidentate fashion. Magnetic and reflectance spectral studies reveal the existence of different stereochemistries for the $Co(II)$, $Ni(II)$ and $Cu(II)$ complexes. The formation of the complexes in solution has been studied conductometrically and spectrophotometrically.

The reported activity of transition metal complexes of thiosemicarbazone and its derivatives against smallpox¹, virus diseases² and certain types of tumours³, prompted us to investigate the complexes containing this type of ligands. In continuation of our previous work⁴⁻⁶, we now report the preparation and characterization of some bivalent metal complexes derived from *p*-chloro- and *p*-methoxybenzylidene-4-phenylthiosemicarbazone (H_2CBPT , H_2MBPT , structures I, II).



Materials and Methods

All the chemicals used were of AR grade. The ligands were prepared by heating equimolar amounts of the aldehyde (4-chlorobenzaldehyde or 4-methoxybenzaldehyde) and 4-phenylthiosemicarbazide in EtOH under reflux for 1/2 hour. The products formed on cooling were filtered off, recrystallized from EtOH and finally dried *in vacuo* over anhydrous $CaCl_2$. The purity was checked by elemental analysis (M.P.: H_2CBPT , $200^\circ C$; H_2MBPT , $173^\circ C$).

The solid complexes were prepared by mixing equimolar amounts of both the metal salt and the ligand in EtOH. The mixture was heated under reflux on a water bath for 1-2 hr. The $Co(II)$, $Ni(II)$ and $Zn(II)$ complexes precipitated on adding sodium

acetate as a buffer. The reaction product was filtered immediately while the solution was still hot, washed with hot EtOH and Et_2O and dried and preserved *in vacuo* over silica gel. The yield was 50-60%.

Infrared (nujol) and reflectance spectra were recorded on Pye Unicam SP 2000, Perkin Elmer 1430, Rotion and Pye Unicam SP 1800 spectrophotometers. However, the spectrophotometric studies in solution were recorded on a J.Y. 201 spectrophotometer. The values of conductance were measured using a Tacussel Type CD6NG conductivity bridge. Magnetic moments were determined using the Gouy method. Elemental analyses (Table 1) were carried out in our laboratory.

Results and Discussion

The complexes $Hg(H_2CBPT)Cl_2 \cdot 2H_2O$, $Cu(H_2CBPT)_2Ac_2$, $M(HL)X \cdot nH_2O$ ($M = Cu$ or Hg ; $X = Cl$ or Ac and $n = 0-1$) and $M(HL)_2 \cdot nH_2O$ ($M = Co, Ni$ or Zn ; $n = 0-2$ and $HL = HCBPT$ or $HMBPT$) were isolated. The analytical results with some physical properties are compiled in Table 1. Attempts to prepare the monoligand complexes of $Co(II)$ and $Ni(II)$ were unsuccessful. The molar conductivities of the complexes in DMF, DMSO or acetonitrile (CH_3CN) at $25^\circ C$ were in the range $1.3-12.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating⁷ their non-electrolytic nature except for $Hg(H_2CBPT)Cl_2 \cdot 2H_2O$ which exhibited a value of $28.1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ which is lower than that reported for 1:1 electrolytes in DMF and may indicate some ionic dissociation in solution due to solvolysis⁸.

The IR spectra of H_2CBPT and H_2MBPT (Table 2) show two strong bands in the $3340-3320$

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Table 1—Analytical Data and Other Physical Properties of the Complexes

Compound	Colour (m.p., °C)	Found (Calc.) (%)				μ_{eff}
		C	H	M	Cl	
Co(HCBPT) ₂ ·2H ₂ O	Brown (146)	50.17 (50.01)	3.41 (3.89)	8.6 (8.76)	—	2.32
Co(HMBPT) ₂ ·2H ₂ O	Brown (168)	55.02 (54.29)	5.11 (4.86)	8.3 (8.88)	—	4.85
Ni(HCBPT) ₂	Brown (243)	52.41 (52.86)	3.27 (3.49)	9.7 (9.23)	—	Diam.
Ni(HMBPT) ₂	Brown (232)	57.74 (57.43)	4.92 (4.50)	9.77 (9.36)	—	Diam.
Cu(HCBPT)Cl·H ₂ O	Green (170)	40.9 (41.40)	2.50 (3.23)	16.20 (15.66)	9.35 (8.74)	—
Cu(HMBPT)Cl ₂	Deep grey (210)	47.5 (47.00)	2.85 (3.68)	16.00 (16.57)	8.50 (9.25)	0.55
Cu(H ₂ CBPT) ₂ Ac ₂	Green (147)	50.13 (50.50)	3.99 (3.97)	8.30 (8.35)	—	2.12
Cu(HMBPT)Ac	Green (135)	50.55 (50.17)	3.66 (4.21)	14.74 (15.61)	—	1.86
Zn(HCBPT) ₂	Yellowish white (208)	52.93 (52.32)	3.43 (3.45)	11.24 (10.17)	—	—
Zn(HMBPT) ₂	Yellow (158)	57.40 (56.83)	4.97 (4.45)	10.31 (10.31)	—	—
Hg(H ₂ CBPT)Cl ₂ ·2H ₂ O	White (158)	27.28 (28.17)	2.52 (2.70)	33.00 (33.52)	—	—
Hg(HMBPT)Cl·H ₂ O	Yellow (163)	34.56 (33.49)	3.17 (2.81)	37.0 (37.19)	—	—

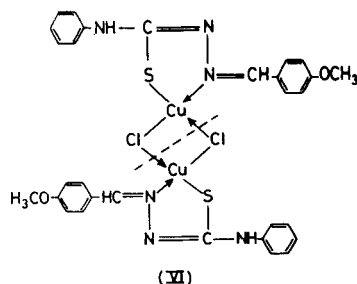
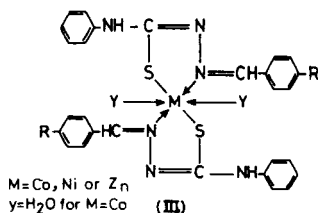
Table 2—Important IR Bands of the Ligands and the Complexes

Compound	$\nu(\text{N}^4\text{H})$	$\nu(\text{N}^2\text{H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{N}^*)$	$\nu(\text{C}=\text{S})$	(N-N)	$\nu(\text{C}-\text{S})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{X})$
H ₂ CBPT	3320	3140	1570	—	775	1010	—	—	—	—
Co(HCBPT) ₂ ·2H ₂ O	3420	—	1560	1620	—	1015	670	465	360	—
Ni(HCBPT) ₂	3400	—	1555	1610	—	1012	655	440	360	—
Cu(HCBPT)Cl·H ₂ O	3320	—	1550	1630	—	1015	670	460	350	270
Zn(HCBPT) ₂	3410	—	1545	1600	—	1015	655	475	370	—
Cu(H ₂ CBPT) ₂ Ac ₂	3310	3135	1570	—	770	1015	—	470	380	—
Hg(H ₂ CBPT)Cl ₂ ·2H ₂ O	3280	3140	1570	—	765	1020	—	485	415	290
H ₂ MBPT	3340	3150	1595	—	785	1025	—	—	—	—
Co(HMBPT) ₂ ·2H ₂ O	3370	—	1585	1605	—	1030	670	450	365	—
Ni(HMBPT) ₂	3350	—	1575	1615	—	1030	640	430	400	—
Cu(HMBPT)Ac	3320	—	1575	1595	—	1030	630	440	360	—
[Cu(HMBPT)Cl] ₂	3330	—	1590	1615	—	1030	645	445	360	250
Zn(HMBPT) ₂	3370	—	1590	1605	—	1030	630	440	370	—
Hg(HMBPT)Cl·H ₂ O	3350	—	1590	1610	—	1035	635	435	375	—

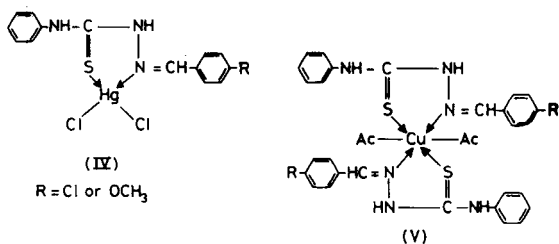
and 3150-3140 cm^{-1} regions which may be assigned to $\nu(\text{N}^4\text{H})$ and $\nu(\text{N}^2\text{H})$ vibrations, respectively^{6,9}. The band observed in the 1590-1570 cm^{-1} region may be due to $\nu(\text{C}=\text{N})$, while that appearing at $\sim 1010 \text{ cm}^{-1}$ is due to $\nu(\text{N}-\text{N})$ ¹⁰. The thione (C=S) group having an adjacent amino proton is relatively unstable and tends to tautomerize¹¹ to the thiol (C-SH) form. However, the spectra of the ligands exhibit two bands in the 1270-1230 and 785-775 cm^{-1} regions due to $\nu(\text{N}=\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ vibrations, while the two bands at ~ 1540

and $\sim 1490 \text{ cm}^{-1}$ may be assigned to $\nu(\text{N}-\text{C}=\text{S})$ vibrations¹². The absence of $\nu(\text{SH})$ band at 2600-2500 cm^{-1} indicates that the ligands exist in thione form (I). Electrical conductance values confirmed the liberation of H^+ ions during the formation of most complexes.

The ligands (H₂CBPT and H₂MBPT) coordinate via the azomethine and thioenol groups in all the metal complexes, except for Cu(H₂CBPT)₂Ac₂ and Hg(H₂CBPT)Cl₂·2H₂O. The disappearance of the $\nu(\text{N}^2\text{H})$ band, the appearance of a new $\nu(\text{C}=\text{N})$



band at $\sim 1610\text{ cm}^{-1}$, a negative shift ($10\text{-}15\text{ cm}^{-1}$) of the $\nu(\text{C}=\text{N})$ band of the thiosemicarbazone residue, a positive shift ($\sim 10\text{ cm}^{-1}$) of the (N-N) band, the appearance of a new $\nu(\text{M}-\text{N})$ band¹³ at $425\text{-}410\text{ cm}^{-1}$, the lack of $\nu(\text{C}=\text{S})$ bands and the appearance of the new $\nu(\text{C}-\text{S})$ ¹⁴ and $\nu(\text{M}-\text{S})$ ¹⁵ bands at $650\text{-}640$ and $475\text{-}440\text{ cm}^{-1}$, respectively, suggest the involvement of both (C=N) and (C-S) groups in the coordination as shown in structure (III) for Co(II), Ni(II) and Zn(II) complexes of the type $\text{M}(\text{HL})_2 \cdot n\text{H}_2\text{O}$. In the case of $\text{Cu}(\text{H}_2\text{CBPT})_2\text{Ac}_2$ and $\text{Hg}(\text{H}_2\text{CBPT})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, the coordination of the neutral ligand through (C=N) and (C=S) groups is supported by the negative shift in the $\nu(\text{C}=\text{S})$ bands, the appearance of a new $\nu(\text{M}-\text{S})$ ¹⁵ band at $485\text{-}470\text{ cm}^{-1}$, the positive shift ($5\text{-}10\text{ cm}^{-1}$) in the $\nu(\text{N}-\text{N})$, the negative shift ($10\text{-}20\text{ cm}^{-1}$) in $\nu(\text{C}=\text{N})$, the appearance of a new $\nu(\text{M}-\text{N})$ ¹³ band at $415\text{-}380\text{ cm}^{-1}$, the appearance of a new $\nu(\text{M}-\text{Cl})$ ¹⁶ band at 290 cm^{-1} in the spectrum of Hg(II) complex. All these evidences suggest structures IV and V for the two complexes $\text{Hg}(\text{H}_2\text{CBPT})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{H}_2\text{CBPT})_2\text{Ac}_2$ respectively.



A monodentate and/or bidentate¹⁴ nature of the acetate group in $\text{Cu}(\text{H}_2\text{CBPT})_2\text{Ac}_2$ [ν_{as} (1530), ν_{s} (1435 cm^{-1})] and $\text{Cu}(\text{HMBPT})\text{Ac}$ [ν_{as} (1510), ν_{s} (1350 cm^{-1})] is indicated by the differences of 95 and 160 cm^{-1} between the two bands. The spectra of $\text{Co}(\text{HCBPT})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{HMBPT})_2 \cdot 2\text{H}_2\text{O}$, exhibit the characteristic bands of the coordinated water at ~ 3480 (ν_{OH}), ~ 1630 ($\delta_{\text{H}_2\text{O}}$), $905\text{-}480$ ($\rho_{\text{r}}\text{H}_2\text{O}$) and $760\text{-}675\text{ cm}^{-1}$ ($\rho_{\text{w}}\text{H}_2\text{O}$)¹⁷. The IR spectrum of $[\text{Cu}(\text{HMBPT})\text{Cl}]_2$ shows a band at 250 cm^{-1} which may be due to $\nu(\text{M}-\text{Cl})$ vibration¹⁶. Its molecular weight determination (Mol. Wt = 801) by the Rast's method¹⁸ suggests dimeric structure (VI).

The values of the apparent formation constants calculated by the continuous variation method¹⁹ were found to be 0.11×10^{12} and $0.51 \times 10^{12}\text{ mol}^{-1}$ for the $\text{CuCl}_2\text{-H}_2\text{CBPT}$ and $\text{CuCl}_2\text{-H}_2\text{MBPT}$ systems, respectively (1:2 complexes) in ethanolic solution. The lower value for $\text{CuCl}_2\text{-H}_2\text{CBPT}$ system may be justified in terms of the inductive effect.

The $\mu_{\text{eff.}}$ value (2.32 B.M.) for $\text{Co}(\text{HCBPT})_2 \cdot 2\text{H}_2\text{O}$ and the appearance of the reflectance spectral band at $14,706\text{ cm}^{-1}$ suggest a low-spin octahedral geometry²⁰. The reflectance spectrum of $\text{Co}(\text{HMBPT})_2 \cdot 2\text{H}_2\text{O}$ shows three bands at 15560 , 19600 and 24600 cm^{-1} which may be assigned to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ and $\text{Co} \rightarrow \text{HCBPT}$ charge-transfer²⁰ transitions, respectively, in a high-spin octahedral structure. This assignment is further supported²¹ by the $\mu_{\text{eff.}}$ value of 4.85 B.M. at room temperature.

The reflectance spectra of $\text{Ni}(\text{HCBPT})_2$ and $\text{Ni}(\text{HMBPT})_2$ exhibit two bands in the $16800\text{-}17000$ and $26700\text{-}27600\text{ cm}^{-1}$ regions, which may be assigned to ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively, in a square-planar geometry. Their diamagnetic nature supports this stereochemistry.

The subnormal $\mu_{\text{eff.}}$ value of 0.55 B.M. for $[\text{Cu}(\text{HMBPT})\text{Cl}]_2$ may be attributed to copper-copper interaction²² in the dimeric structure. The spectrum of the $[\text{Cu}(\text{HMBPT})\text{Cl}]_2$ shows an intense band at 17667 cm^{-1} and a broad band at 24875 cm^{-1} . The former indicates a pseudotetrahedral stereochemistry, while the latter may be ascribed to charge-transfer, probably $\text{Cl} \rightarrow \text{Cu}$ ²³. The reflectance spectrum of $\text{Cu}(\text{HMBPT})\text{Ac}$ shows two bands at 14350 and 26400 cm^{-1} which are characteristic of the tetrahedral environment around the Cu(II) ion²⁴. The $\mu_{\text{eff.}}$ value (1.86 B.M.) excludes a polymeric structure and shows no copper-copper interaction. Finally, the magnetic moment of $\text{Cu}(\text{H}_2\text{CBPT})_2\text{Ac}_2$ corresponds to the presence of only one unpaired electron. However, from magnetic moment data, the characterization of the stereochemistry of Cu(II) complexes is not always possible. The reflectance spectrum shows two bands at

16850 and 15667 cm^{-1} which may be due to the ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions. The positions and the band shapes indicate tetragonally distorted octahedral stereochemistry²¹. The band at 23250 cm^{-1} is assumed to be due to M \rightarrow L charge-transfer.

It is interesting to note that the ligand, HMBPT⁻, acts as a strong field ligand while HCBPT⁻ behaves as a weak field ligand in cobalt(II) complexes. The presence of a methoxy group in the benzene ring enhances the electron density on coordination sites and increases the value of 10 *Dq* giving a low-spin state, while the presence of the chloro group (electron withdrawing) diminishes the same and hence decreases the 10 *Dq* yielding a high-spin configuration.

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