

Chelates of Thiocarbohydrazone Derivatives: Part I—Complexes of Mn(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II) & Pb(II) with 1,5-Bis(salicylidene)thiocarbohydrazone

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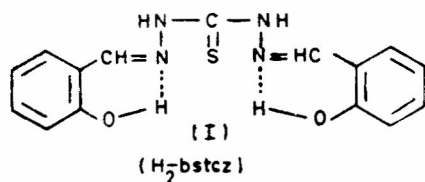
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Complexes of Mn(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II) and Pb(II) with 1,5-bis(salicylidene)thiocarbohydrazone (H_2 -bstcz) of the types $M(bstcz).nH_2O$ (where $M = Mn, Ni, Cu, Zn$ or Pd ; $n = 1, 2$ or 3), $Cu(H-bstcz)(CH_3COO)$ and $M_2(bstcz)(CH_3COO)_2.nH_2O$ (where $M = Cd(II)$ or $Pb(II)$; $n = 2$ or 0) have been prepared and characterized on the basis of analytical, spectral and magnetic moment data. The complex, $Ni(bstcz).nH_2O$ has been isolated in two forms, a four-coordinated diamagnetic and a six-coordinated paramagnetic form. Ni(II) (diamagnetic) and Pd(II) complexes have been assigned square-planar structures, Zn(II) complex tetrahedral, Cu(II) complex distorted octahedral and the acetato complexes of Pb(II) and Cd(II) have been assigned dimeric structures.

METAL chelates of Schiff bases have been a subject of extensive investigations during the last two decades^{1,2}. Ablov *et al.*^{3,4} and others⁵⁻¹⁰ have studied metal complexes of Schiff bases derived from salicylaldehyde or substituted salicylaldehydes and semicarbazide or thiosemicarbazide. Kurzer and Wilkinson have reviewed¹¹ the complexes of thiocarbohydrazone, carbohydrazone and their derivatives. From the survey of the existing literature, it appears that the complexing behaviour of 1,5-bis(salicylidene)thiocarbohydrazone (H_2 -bstcz) (I) has not been investigated, hitherto.



H_2 -bstcz is a potential pentadentate dibasic Schiff base and is expected to form mononuclear as well as dinuclear complexes with metal ions. In view of its coordinating flexibility, it was thought worthwhile to investigate the complexes of bivalent metal ions with H_2 -bstcz. In the present paper, we report complexes of Mn(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II) and Pb(II) with H_2 -bstcz.

Materials and Methods

All the chemicals and solvents used were either E. Merck (extra pure) or BDH (AR) reagents and were used without further purification.

H_2 -bstcz was prepared as reported previously¹² and recrystallized from acetone as colourless plates; m.p. 192-93° (d), lit.¹² m.p. 190° (d).

Preparation of complexes: $M_2(bstcz)(CH_3COO)_2.nH_2O$ ($M = Cd, n = 2$; $M = Pb, n = 0$)—The ligand (0.01 mole) was dissolved in 50 ml of acetone-ethanol (3:2, v/v) and the solution added dropwise to the metal acetate hydrate (0.02 mole) dissolved in 50 ml of ethanol-acetone mixture (2:1, v/v). A voluminous precipitate of metal complex separated almost quantitatively. It was filtered, washed with ethanol four times and dried *in vacuo* over $CaCl_2$.

$M(bstcz).H_2O$ ($M = Mn, Zn$)—The ligand solution (0.01 mole in 50 ml of acetone-ethanol) was mixed with metal acetate hydrate (0.01 mole) dissolved in 50 ml of aq. ethanol and refluxed on a steam-bath for 30 min. A precipitate separated on adding water (50 ml). It was filtered, washed with a large volume of water and dried *in vacuo* over $CaCl_2$.

$Pd(bstcz).H_2O$ —Aqueous solution (1%) of $PdCl_2$ (pH 3-4) was added to an equimolar solution of the ligand in acetone-ethanol. The contents were digested on a steam-bath for 30 min when a chocolate-brown precipitate separated. It was filtered, washed with water and ethanol and dried *in vacuo* over $CaCl_2$.

$Cu(H-bstcz)(CH_3COO)$ —Cupric acetate dihydrate (0.01 mole) dissolved in ethanol (40 ml) containing 3-5 ml acetic acid was added to the ligand solution (0.01 mole in acetone-ethanol). It was refluxed on a steam-bath for 30 min when a dark-brown precipitate separated out. It was filtered, washed with ethanol and dried *in vacuo* over $CaCl_2$.

$Cu(bstcz).2H_2O$ — Cupric chloride dihydrate (0.01 mole) dissolved in ethanol (30 ml) was mixed with the ligand solution (0.01 mole in acetone-ethanol) and refluxed on a steam-bath for 30 min. A yellowish-green precipitate separated out when the resulting solution was diluted with excess of water containing a few drops of dilute NH_4OH . It was filtered, washed with aqueous ethanol four times and dried *in vacuo* over $CaCl_2$.

$Ni(bstcz).H_2O$ — A solution of $NiCl_2.6H_2O$ (0.01 mole) in 50 ml ethanol was treated with an equimolar amount of the ligand solution (in acetone-ethanol) and heated on a steam-bath for 15-20 min. The pH of the mixture was raised to 6-7 by adding 2-3 ml of β -picoline or pyridine when an orange-red solution was obtained. From the resulting solution, the complex was separated by adding about 200 ml of water. The precipitate was digested on a steam-bath for 30 min, filtered, washed thoroughly with water and dried *in vacuo* over $CaCl_2$.

$Ni(bstcz).3H_2O$ — A solution of $NiCl_2.6H_2O$ (0.01 mole in 50 ml aq. ethanol) was treated with an equimolar amount of the ligand solution (0.01 mole in acetone-ethanol) and refluxed on a steam-bath for 30 min. The mixture was treated with an aqueous solution of CH_3COONa with constant stirring when a greyish-brown precipitate separated out quantitatively. It was filtered, washed thoroughly with water and ethanol and dried *in vacuo* over $CaCl_2$.

The conductance measurements were carried out at room temperature in DMF solution using a LBR type conductivity bridge. The magnetic susceptibility measurements were carried out using the Gouy method and employing $Hg[Co(NCS)_4]$ as standard. The IR spectra were recorded in nujol on Perkin-Elmer 237 and 631 spectrophotometers. The electronic spectra were recorded in nujol using a Cary-14 spectrophotometer.

Results and Discussion

The analytical results (Table 1) indicate that the complexes with H_2 -bstcz are of three types:

(a) $M(bstcz).nH_2O$ (where $M = Mn, Ni, Cu, Zn$ and Pd ; $n = 1, 2$ or 3), (b) $Cu(H-bstcz)(CH_3COO)$, and (c) $M_2(bstcz)(CH_3COO)_2.nH_2O$ (where $M = Cd$ or Pb ; $n = 2$ or 0).

The hydrated complexes of $Mn(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ are slightly soluble in ethanol or acetone but dissolve appreciably in DMF and polar solvents. The DMF solutions of complexes are almost non-conducting indicating their non-ionic nature. The acetato complexes of $Cu(II)$, $Pb(II)$ and $Cd(II)$ are almost insoluble in water and organic solvents. The complexes of $Cu(II)$, $Zn(II)$, $Pd(II)$ and $Cd(II)$ become anhydrous when heated at 100° . On the basis of the insolubility and analytical data of $Cd(II)$ and $Pb(II)$ complexes, it appears that they are dinuclear complexes involving the ligand molecules as bridges.

In the case of $Ni(II)$, two forms of complexes have been isolated. One is yellowish-brown diamagnetic compound, $Ni(bstcz).H_2O$ and the other is paramagnetic greyish-brown complex of composition $Ni(bstcz).3H_2O$. The former dehydrates below 100° indicating the non-coordinated nature of the water molecule whereas the latter, on heating, still retains two water molecules which are probably coordinated.

It is found that the greyish-brown form of nickel (II) complex exhibits magnetic moment of 2.34 B.M. at room temperature which is low for octahedral or tetrahedral $Ni(II)$ complexes. Paramagnetism of greyish-brown form may be attributed to the formation of dimeric octahedral species, $[Ni_2(bstcz)_2].6H_2O$ or water coordinated octahedral species $[Ni(bstcz)(H_2O)].2H_2O$, associated with a small amount of the diamagnetic monomer^{1,13-15}. Yellowish-green $Cu(II)$ complex, $[Cu(bstcz)].2H_2O$ exhibits magnetic moment value close to spin-only value for one unpaired spin (~ 1.76 B.M.) at room temperature. As the magnetic susceptibility of the complex was not determined below room temperature, nothing can be said about the presence or absence of

TABLE 1 — ANALYTICAL AND MAGNETIC MOMENT DATA (AT $295^\circ K$) OF THE COMPLEXES

Complex	Found (Calc.), %				% loss of H_2O at 100°	μ_{eff} (B.M.)
	C	H	N	M		
$[Mn(bstcz).H_2O]$	46.82 (46.77)	3.50 (3.66)	14.38 (14.54)	14.18 (14.26)	—	5.34
$[Ni(bstcz)].H_2O$	46.06 (46.31)	3.72 (3.63)	14.31 (14.40)	15.12 (15.09)	4.63 (4.63)	Diamag.
$[Ni(bstcz)(H_2O)].2H_2O$	42.48 (42.38)	4.20 (4.27)	13.02 (13.18)	13.90 (13.81)	4.24 (4.23)	2.34
$[Cu(bstcz)].2H_2O$	43.58 (43.74)	3.82 (3.91)	13.48 (13.60)	15.29 (15.43)	8.74 (8.73)	1.76
$[Cu(H-bstcz)(CH_3COO)]$	46.64 (46.79)	3.58 (3.70)	12.71 (12.85)	14.46 (14.57)	—	1.03
$[Zn(bstcz)].H_2O$	45.34 (45.53)	3.62 (3.57)	14.02 (14.16)	16.43 (16.52)	4.55 (4.54)	Diamag.
$[Pd(bstcz)].H_2O$	41.08 (41.25)	3.31 (3.23)	12.78 (12.83)	24.30 (24.36)	4.12 (4.12)	do
$[Cd_2(bstcz)(CH_3COO)_2].2H_2O$	32.86 (33.02)	3.08 (3.21)	8.05 (8.11)	32.52 (32.46)	5.21 (5.20)	do
$[Pb_2(bstcz)(CH_3COO)_2]$	26.96 (27.01)	2.08 (2.15)	6.82 (6.63)	48.95 (49.05)	—	do

magnetic exchange. Dark-brown complex $\text{Cu}(\text{H-bstcz})(\text{CH}_3\text{COO})$ displays a subnormal magnetic moment value (1.03 B.M.) at room temperature which suggests that the compound has dimeric structure in which magnetic exchange takes place probably by means of overlap of the dx^2-y^2 orbitals¹⁶⁻¹⁸.

The diamagnetic Ni(II) and Pd(II) complexes, $[\text{M}(\text{bstcz})]_2\text{H}_2\text{O}$ may be assigned square-planar structures.

Mn(II) complex, $[\text{Mn}(\text{bstcz})\text{H}_2\text{O}]$ shows a slightly lower magnetic moment value (5.34 B.M.) than that expected for the high-spin octahedral Mn(II) ion¹. The low magnetic moment values of Schiff base complexes of Mn(II) have been reported previously also and attributed to spin exchange in solid phase or due to the formation of some Mn(III) species¹.

Electronic spectra — The electronic spectra of the complexes are of little help in the present case since the $d-d$ transitions are masked in most of the cases by strong charge-transfer bands. The complexes display three or four bands around 230, 260, 310-350, 370-390, and 420-440 nm due to charge-transfer and intraligand $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions. The band around 420 ± 15 nm in the spectra of the complexes, which is not present in the ligand spectrum, may be assigned as a ligand to metal charge-transfer band. In the case of yellowish-green Cu(II) complex, $[\text{Cu}(\text{bstcz})]_2\text{H}_2\text{O}$, a broad shoulder near 740 nm is observed which is assigned to the transition ${}^2E_g \rightarrow {}^2T_{2g}$ in distorted octahedral field^{19,20}. The greyish-brown variety of Ni(II) complex does not show any $d-d$ bands, probably these are obscured by extended tail of charge-transfer band. However, the yellowish-brown variety exhibits a strong $d-d$ band at 465 nm. This band is assigned to the transition ${}^1A_{1g} \rightarrow {}^1B_{1g}$ as observed for square-planar Ni(II) complexes^{6,21}.

Infrared spectra — The ligand exhibits a strong and broad band in the range 3180-3145 cm^{-1} which is attributed to a combination of $\nu\text{N-H}$ and νOH frequencies. It is reasonable to expect hydrogen bonding between phenolic hydrogen atoms and the hydrazone $\text{C}=\text{N}$ nitrogen atoms on the basis of the broadening of this band and magnitude of shift from the normal position of the free phenolic $\nu\text{O-H}$ vibration (3700-3500 cm^{-1})^{22,23}. Further, this band disappears in all the complexes except $\text{Cu}(\text{H-bstcz})(\text{CH}_3\text{COO})$, indicating that phenolic (OH) groups of $\text{H}_2\text{-bstcz}$ get deprotonated in metal complexes^{18,22}. Weak and broad bands observed around 3200 and 3060 cm^{-1} are assigned to asymmetric and symmetric $\nu\text{N-H}$ vibrations, respectively²². The IR spectra of all the hydrated complexes exhibit a weak and broad band in the range 3550-3300 cm^{-1} indicating the presence of associated water molecules in the complexes. The occurrence of a new band at 860 cm^{-1} only in the case of Mn(II) complex suggests the coordination of water molecule in this complex²⁴. The acetato complex of Cu(II) exhibits a strong band at 3215 cm^{-1} due to free phenolic (OH) group. Thus, in the case of $\text{Cu}(\text{H-bstcz})(\text{CH}_3\text{COO})$, the IR spectrum indicates that at least one of the phenolic groups is not involved in coordination with Cu(II).

The ligand spectrum shows a band at 1625 cm^{-1} assignable to $\nu\text{C}=\text{N}$ vibration^{25,26}. This band shifts

to lower frequency by 15 to 25 cm^{-1} in the complexes of Cd(II), Pb(II), Mn(II) and in $\text{Ni}(\text{bstcz})_2\cdot 3\text{H}_2\text{O}$. The shift of $\nu\text{C}=\text{N}$ band to lower frequency side is attributed to coordination through both the azomethine nitrogens of the ligand²⁵. The IR spectra of Cu(II), Zn(II), Pd(II) and diamagnetic Ni(II) complexes exhibit splitting of $\nu\text{C}=\text{N}$ vibration into two bands, one band is located at the original position (1623 ± 2 cm^{-1}) and the other at a lower frequency (1605 ± 5 cm^{-1}) indicating that one of the $\text{C}=\text{N}$ groups is not involved in coordination²⁷. Three bands observed at 1565, 1540 and 1492 cm^{-1} are attributed to phenyl ring $\nu\text{C}=\text{C}$, $\nu\text{C}-\text{N}$ and $\delta\text{N}-\text{H}$ vibrations^{28,32} respectively. Except Cu(II) complex, $\text{Cu}(\text{H-bstcz})(\text{CH}_3\text{COO})$, all the other complexes exhibit only two bands in this region.

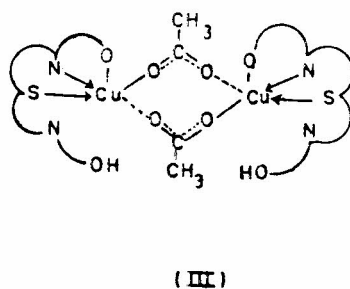
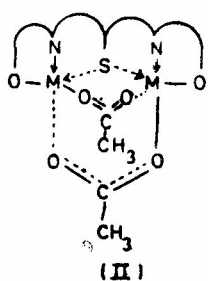
The ligand may be regarded as containing a thioamide group ($-\text{NH}-\text{CS}-$) and therefore it is expected to show the characteristic thioamide bands in the regions $\sim 1550, 1300-1200, 1000$ and $800-750$ cm^{-1} (ref. 29-31). The first thioamide band (at 1540 cm^{-1} in the ligand) which is mainly due to the combination of $\nu\text{C}-\text{N}$ and $\delta\text{N}-\text{H}$ vibrations, shifts to higher frequency side and couples with phenyl ring ($\text{C}=\text{C}$) stretching vibration and is observed as a strong and broad band at 1560 ± 10 cm^{-1} in the complexes³². The second thioamide band (at 1290 cm^{-1} in the ligand) has major contributions from $\nu\text{C}-\text{N}$ and $\nu\text{C}=\text{S}$ vibrations. It splits up into two bands in the IR spectra of the complexes which are observed at 1300 ± 10 cm^{-1} and 1260 ± 5 cm^{-1} . A strong and sharp band at 960 cm^{-1} in the free ligand, having major contributions from $\nu\text{C}-\text{N}$ and δCNN and a minor contribution from $\nu\text{C}=\text{S}$ vibration, splits into two or three weak bands in all the complexes. The fourth thioamide band (at 782 cm^{-1} in the ligand) which is mainly due to $\nu\text{C}=\text{S}$ vibration^{33,34} shifts to lower frequency and is observed as a weak band at 730 ± 5 cm^{-1} in the mononuclear complexes and at 720 ± 2 cm^{-1} in the dinuclear complexes. Thus, these shifts of thioamide bands clearly indicate that sulphur atom of the thione group ($\text{C}=\text{S}$) of the ligand is involved in coordination in all the complexes. A medium to strong band observed at 1330 cm^{-1} in the free ligand, attributed to in-plane deformation vibration³⁵ of OH, disappears in the spectra of metal complexes. But in the case of acetato complex of Cu(II), a medium band is observed near the same position (1328 cm^{-1}) as in the ligand indicating that one of the phenolic (OH) groups is not involved in coordination. The next strong band in the spectrum of the ligand observed at 1182 cm^{-1} may be assigned to $\nu\text{C}-\text{O}$ of the hydrogen bonded ring system, which shifts to higher frequency side (1208 ± 10 cm^{-1}) in metal complexes. This assignment is purely tentative since the assignment of $\nu\text{C}-\text{O}$ band is still in controversy^{36,37}.

The IR spectrum of Cu(II) complex, $\text{Cu}(\text{H-bstcz})(\text{CH}_3\text{COO})$, exhibits two bands at 1168 and 1215 cm^{-1} for both, free and coordinated $\nu\text{C}-\text{O}$ vibrations. This acetato complex also exhibits strong and broad νCOO vibrations at 1545 and 1445 cm^{-1} , indicating the presence of bridging acetate group like that in Cu(II) acetate²⁴. The IR spectrum of $[\text{M}_2(\text{bstcz})$

$(\text{CH}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$ also exhibits νCOO vibrations at 1545 and 1470 cm^{-1} indicating the bridging nature of acetate group²⁴.

Some other medium to strong bands observed at 1382, 1162, 1042 and 802 cm^{-1} in the free ligand show negligible shifts but get intensified in the spectra of complexes. The IR spectra of complexes exhibit several bands in the region 650-200 cm^{-1} . A band near 650 cm^{-1} in the complexes is assigned to $\nu\text{M}-\text{O}$ vibration³⁸ which shifts to lower frequency side with increasing mass of the metal atom³⁹. Two new bands observed in the spectra of the complexes in the ranges 410-380 and 345-300 cm^{-1} are suggested to be due to $\nu\text{M}-\text{N}$ and $\nu\text{M}-\text{S}$ vibrations^{40,41} respectively.

On the basis of the foregoing results the complexes $[\text{M}(\text{bstcz})] \cdot \text{H}_2\text{O}$ ($\text{M}=\text{Ni}$ and Pd) have been assigned square-planar; $[\text{Zn}(\text{bstcz})] \cdot \text{H}_2\text{O}$, a tetrahedral; $[\text{Cu}(\text{bstcz})] \cdot 2\text{H}_2\text{O}$, a distorted octahedral; and $[\text{Ni}(\text{bstcz})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ and $[\text{Mn}(\text{bstcz})\text{H}_2\text{O}]$, octahedral structures. The complexes, $[\text{M}_2(\text{bstcz})(\text{CH}_3\text{COO})_2] \cdot n\text{H}_2\text{O}$ and $\text{Cu}(\text{H-bstcz})(\text{CH}_3\text{COO})$ are assigned dimeric structures (II) and (III) respectively. In planar,



tetrahedral or distorted octahedral complexes the ligand behaves as quadridentate whereas it acts as a pentadentate ligand in octahedral or dinuclear complexes and tridentate in $\text{Cu}(\text{H-bstcz})(\text{CH}_3\text{COO})$.

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