

Preparation and characterization of vanillin thiosemicarbazone complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)

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Abstract. Complexes of vanillin thiosemicarbazone (3-methoxy-4-hydroxybenzaldehyde thiosemicarbazone), (VTSCH) with several divalent metal ions have been isolated. Structures have been assigned to these complexes based on electrical conductivity, magnetic susceptibility and spectroscopic measurements.

Keywords. Vanillin thiosemicarbazone complexes; electrical conductance; magnetic susceptibility; spectral studies.

1. Introduction

The thiosemicarbazones of substituted benzaldehydes show marked differences in their donor properties and biological activities compared to that of unsubstituted benzaldehyde. Vanillin thiosemicarbazone has long been studied for its fungicidal and antitubercular activities (Paulo da Silva Lacaz *et al* 1958). It has also been tested as a reagent for metal ions. Apart from these, structural studies on the metal derivatives of this thiosemicarbazone, however, have not been carried out so far.

2. Experimental

2.1 Reagents

Vanillin thiosemicarbazone was prepared by refluxing recrystallised thiosemicarbazide with vanillin (1 : 1 ratio) in ethanol for 2 hr.

2.2 Preparation of the complexes

The complexes of Co(II), Ni(II) and Cu(II) were prepared by adding a hot aqueous solution of the respective metal acetate or chloride, dropwise, to a refluxing methanolic solution of the ligand containing sodium acetate (1 g) until the metal-to-ligand ratio reached 1 : 2 (in copper complex the ratio was 1 : 1). The solid separated was filtered out, washed with water and then with methanol and dried over P_4O_{10} .

The halide complexes of Zn(II), Cd(II) and Hg(II) were prepared by adding methanolic solutions of the respective metal halide to refluxing methanolic solution of the ligand. The reaction mixture was maintained at the refluxing temperature for 3 hr.

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The chloride and bromide complexes of Cd(II) and Hg(II) separated as yellow solids. The other complexes were obtained by concentrating the resulting solutions and by subsequent cooling of the viscous mass obtained. The complexes were filtered, washed with small quantities of methanol and dried over P_4O_{10} .

2.3 Physical methods and analysis

Molar conductances of the complexes in methanol and nitrobenzene ($ca\ 10^{-3}\ M$) were determined at $28 \pm 2^\circ C$ using an Elicos conductance bridge. The magnetic susceptibilities were determined by Gouy method at room temperature. The electronic spectra were recorded in methanol on a Shimadzu recording spectrophotometer SP200. IR spectra (KBr disc) were recorded on a Perkin-Elmer 397 spectrophotometer.

The metal, sulphur and halogens in the complexes were determined by standard procedures (Vogel 1978). Carbon, hydrogen and nitrogen were determined by microanalysis.

3. Results and discussion

The analytical data (table 1) show that the complexes have the formulae: $M(vtsc)_2$, where $M = Co$ or Ni ; $[Cu(vtsc)Cl] \cdot H_2O$; $Zn(vtSCH)_2 X_2$, where $X = Cl$ or Br ; $Zn(vtSCH)_4 I_2$; $Cd(vtSCH)_2 X_2$, where $X = Cl, Br$ or I and $Hg(vtSCH)X_2$, where $X = Cl, Br$ or I .

3.1 Electrical conductance

The cobalt, nickel and copper complexes are non-electrolytes in methanol as well as in nitrobenzene. The Zn(II), Cd(II) and Hg(II) complexes dissociate in methanol, in the concentration range $10^{-3}\ M$. However, these values are much lower than the value expected for 1:2 electrolyte in methanol (Deacon *et al* 1965). Their non-electrolytic nature is confirmed by the molar conductance values in nitrobenzene.

3.2 Magnetic properties

The Co(II) complex gives a magnetic moment of 2.13 BM. This suggests a square planar configuration (Figgis and Lewis 1964). The magnetic susceptibility values obtained for $Ni(vtsc)_2$ indicates that it is diamagnetic and has a square planar configuration. The Cu(II) complex shows a low value (1.09 BM) compared to the spin-only value (1.73 BM). This suggests a polynuclear configuration, i.e. $[Cu(vtsc)Cl]_x \cdot X \cdot H_2O$ facilitating antiferromagnetic exchange (Figgis and Lewis 1964). As expected, all the Zn(II), Cd(II) and Hg(II) complexes are diamagnetic.

3.3 Electronic spectra

The weak broad band at 1050 nm in the absorption spectrum of Co(II) complex is characteristic of square planar geometry (Nishikawa and Yamada 1964). It also presents a charge-transfer band at 440 nm. The green nickel complex, $Ni(vtsc)_2$ has three bands in its reflectance spectrum. The first two, at 440 and 500 nm may be associated with the charge-transfer processes. The other band observed at 610 nm may be assigned to the $^1A_{1g} \rightarrow ^1B_{1g}$ transition expected for square planar Ni(II) complex

Table 1. Analytical data of vanillin thiosemicarbazone complexes*

Complex	%Metal	%Carbon	%Hydrogen	%Nitrogen	%Sulphur	%Halogen
Co(VTSC) ₂	11.68 (11.61)	43.01 (42.61)	4.17 (3.94)	16.59 (16.57)	12.21 (12.64)	—
Ni(VTSC) ₂	11.56 (11.59)	43.09 (42.63)	4.16 (3.94)	16.77 (16.58)	12.43 (12.64)	—
[Cu(VTSCCl)]·H ₂ O	18.54 (18.62)	31.70 (31.68)	3.18 (3.52)	12.56 (12.32)	9.40 (9.40)	10.27 (10.39)
Zn(VTSC) ₂ Cl ₂	11.10 (11.14)	36.90 (36.85)	3.80 (3.75)	14.55 (14.33)	10.90 (10.93)	12.00 (12.09)
Zn(VTSC) ₂ Br ₂	9.72 (9.68)	31.85 (32.00)	3.25 (3.26)	12.40 (12.44)	9.38 (9.49)	23.80 (23.65)
Zn(VTSC) ₂ I ₂	5.41 (5.36)	35.40 (35.44)	3.64 (3.61)	13.90 (13.78)	10.22 (10.51)	20.40 (20.80)
Cd(VTSC) ₂ Cl ₂	17.70 (17.74)	34.52 (34.12)	3.50 (3.47)	13.38 (13.27)	10.10 (10.12)	11.30 (11.19)
Cd(VTSC) ₂ Br ₂	15.52 (15.56)	29.83 (29.93)	3.08 (3.04)	11.60 (11.64)	8.49 (8.88)	22.02 (22.12)
Cd(VTSC) ₂ I ₂	13.22 (13.77)	26.50 (26.48)	2.65 (2.69)	10.25 (10.30)	7.80 (7.85)	31.00 (31.09)
Hg(VTSC) ₂ Cl ₂	40.00 (40.39)	21.72 (21.76)	2.14 (2.21)	8.40 (8.46)	6.18 (6.45)	14.16 (14.27)
Hg(VTSC) ₂ Br ₂	34.12 (34.25)	18.40 (18.46)	1.80 (1.88)	7.09 (7.18)	5.20 (5.47)	27.32 (27.29)
Hg(VTSC) ₂ I ₂	29.22 (29.52)	15.91 (15.90)	1.65 (1.62)	6.20 (6.18)	4.75 (4.72)	37.30 (37.35)

* Calculated values in parenthesis

(Jorgensen 1962). This is in accordance with the magnetic data. The Cu(II) complex exhibits a broad absorption band at 460 nm which may be attributed to $L \rightarrow M$ charge-transfer transition. Another broad band observed with an absorption maximum at 690 nm is assigned to $d \rightarrow d$ transition. This suggests a square planar geometry for the complex (Campbell 1975; Ajayi and Goddard 1971).

3.4 IR spectra

The IR spectra of the ligand and the complexes were examined in detail. The characteristic IR bands are given in table 2. The strong bands in the spectra between 3520 and 3270 cm^{-1} may be assigned to ν_{NH_2} and ν_{NH} (Haines and Sun 1968; Campbell and Grzeskowiak 1967; Burns 1968). The strong band at 3150 cm^{-1} in the spectrum of the ligand may be due to ν_{OH} . The low frequency shift of this band compared to normal OH vibration band (at 3480 cm^{-1}) (Nakamoto 1963) may be due to hydrogen bonding. The corresponding δOH band appears at 1610 cm^{-1} in the ligand spectrum. The fact that these two bands are retained almost at the same positions excludes any possible participation of the oxygen atom of the phenolic group in coordination. The shifting of the band at 1600 cm^{-1} ($\nu_{\text{C}=\text{N}^3}$) to lower wave number in the complexes indicates the participation of N^3 in coordination (Podder and Saha Nityananda 1975). However, in $\text{Zn}(\text{VTSC})_4\text{I}_2$ this band does not show any appreciable shift and hence there may not be nitrogen coordination. The absence of bands in the region 2650–2500 cm^{-1} in the free ligand indicates the absence of S-H grouping in the free ligand (Bellamy 1978).

After eliminating numerous well-defined bands in the region 940 to 700 cm^{-1} in the spectrum of the ligand, a band of strong intensity at 775 cm^{-1} can be assigned to pure $\nu_{\text{C}=\text{S}}$ (Bellamy 1978). In a set of complexes, $\text{Co}(\text{VTSC})_2$, $\text{Ni}(\text{VTSC})_2$ and $[\text{Cu}(\text{VTSC})\text{Cl}] \cdot \text{H}_2\text{O}$ this band disappears and a new band appears around 660 cm^{-1} (in $\nu_{\text{C}=\text{S}}$ region). These facts are compatible with the enolisation of the $-\text{NH}-\text{C}=\text{S}$ group, in the ligand, to $-\text{N}=\text{C}-\text{SH}$ in the presence of the metal ion and the coordination of the metal ion through the S atom after the elimination of H. In another set of complexes (complexes of Zn(II), Cd(II) and Hg(II) halides) the $\nu_{\text{C}=\text{S}}$ band shifted to lower

Table 2. Characteristic IR bands (cm^{-1}) of vanillin thiosemicarbazone and its complexes

	δOH	νOH	$\nu\text{C}=\text{N}^3$	$\nu\text{C}=\text{S}$	$\nu\text{C}-\text{S}$	$\nu\text{M}-\text{N}$
VTSCH	3150s	1610s	1600vs	775s	—	—
$\text{Co}(\text{VTSC})_2$	3150s	1620s	1580s	—	660m	550m
$\text{Ni}(\text{VTSC})_2$	3150m	1610m	1585s	—	660m	550m
$[\text{Cu}(\text{VTSC})\text{Cl}] \cdot \text{H}_2\text{O}$	3150s	1620s	1590vs	—	650m	540m
$\text{Zn}(\text{VTSCH})_2\text{Cl}_2$	3170s	1615s	1590vs	742m	—	545m
$\text{Zn}(\text{VTSCH})_2\text{BR}_2$	3180s	1620s	1590vs	745m	—	535m
$\text{Zn}(\text{VTSCH})_4\text{I}_2$	3180s	1620s	1600vs	745s	—	—
$\text{Cd}(\text{VTSCH})_2\text{Cl}_2$	3160s	1620s	1590s	745m	—	540m
$\text{Cd}(\text{VTSCH})_2\text{Br}_2$	3180s	1620s	1590vs	745m	—	540m
$\text{Cd}(\text{VTSCH})_2\text{I}_2$	3200s	1615m	1580vs	745m	—	540m
$\text{Hg}(\text{VTSCH})\text{Cl}_2$	3160s	1625s	1590vs	745m	—	540m
$\text{Hg}(\text{VTSCH})\text{Br}_2$	3180s	1625s	1585vs	745m	—	550m
$\text{Hg}(\text{VTSCH})\text{I}_2$	3160s	1620s	1590vs	745m	—	550m

vs = Very strong; s = strong; m = medium

frequency region ($\sim 745 \text{ cm}^{-1}$). However, there are situations where the $\nu_{\text{C=S}}$ band of the ligand is shifted only by $\sim 40 \text{ cm}^{-1}$ in the complexes (Sujuki 1962). Hence, in the present case, the shift of $\nu_{\text{C=S}}$ band in the complexes, eventhough small, indicates coordination through sulphur of $-\text{NH}-\underset{|}{\text{C}}=\text{S}$ group in the ligand (without enolisation). The bands appearing around 550 cm^{-1} in the spectra of the complexes may be assigned to M–N stretching frequencies.

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