

Synthesis and Structural Studies of Complexes of 4'-Methyl Acetophenone *o*-hydroxy 4-Benzamido Thiosemicarbazone with Oxovanadium(IV), Cobalt(II), Nickel(II) and Copper(II)

RAKHI ARORA*, NEELAM SINGH†, SHAKSHI CHAUDHRY† and S.L. VASHIST‡
Chemistry Department, Haryana Engineering College, Jagadhari-135 003, India

Complexes of VO(IV), Co(II), Ni(II) and Cu(II) with 4'-methyl acetophenone *o*-hydroxy-4-benzamido thiosemicarbazone have been isolated and characterised on the basis of analytical data, molar conductance, magnetic susceptibility, electronic and infrared spectral measurements. Vanadyl complexes indicate square pyramidal geometry, while $MLCl_2(H_2O)_2$, $ML(CH_3COO)_2$ [$M=Co(II)$, $Ni(II)$], octahedral; and $[Cu(L)Cl_2H_2O]_2$, polymeric octahedral bridging and $[Cu(CH_3COO)_2L]_2$, square pyramidal geometry around the metal ion, where $L = (C_{17}H_{18}N_4O_2S)$.

Key Words: 4'-Methyl acetophenone *o*-hydroxy 4-benzamido thiosemicarbazone, VO(IV), Co(II), Ni(II), Cu(II) complexes.

INTRODUCTION

Shoukry *et al.*¹ and Satpathy *et al.*² have isolated complexes with ligands containing S, N and O-donor atoms from alkaline and neutral media. The >N—C—S— moiety in these compounds has been responsible for pesticidal³ and fungicidal activities. A literature survey indicates that there is no earlier work on the metal complexes of 4-methyl acetophenone *o*-hydroxy-4'-benzamido thiosemicarbazone, a ligand containing S-, N- and O-donor sites with transition metal ions. Here we report the VO(IV), Co(II), Ni(II) and Cu(II) complexes with the above ligand.

EXPERIMENTAL

All the chemicals used were reagent grade. The preparation of the ligand has been described earlier⁴.

The complexes were prepared by mixing methanolic solutions of 4-methyl acetophenone-*o*-hydroxy-4'-benzamido thiosemicarbazone (1.5 mmol) and the appropriate metal salt (*ca.* 1.5 mmol) and stirring the mixture in a round-bottom

†Chemistry Department, M.M. College, Modinagar, India

‡Department of Chemistry, M.L.N. College, Yamuna Nagar-135 001, India.

flask; it was refluxed for about 2 h on a water bath after raising the pH to 7.0 with sodium hydroxide solution. The complexes precipitated were filtered, washed successively with ethanol and ether and dried *in vacuo*.

Chloride in the complexes was estimated gravimetrically as AgCl, and the metals were analysed by the standard literature procedures, after destroying the organic part first with a mixture of nitric and hydrochloric acids and then with concentrated sulphuric acid. Nitrogen was estimated by micro-analysis, and sulphur as BaSO₄.

Molar conductances of the complexes were measured in 0.001 M nitrobenzene/dimethyl sulfoxide on Elico-conductivity meter. Magnetic susceptibility measurements were carried out at room temperature on a Gou's electro balance using Hg[Co(NCS)₄] as the calibrant. The experimental magnetic moments were corrected by applying diamagnetic corrections. Electronic spectra were recorded on a Cary-4 spectrophotometer, while the IR-spectra were recorded on a Perkin-Elmer spectrophotometer.

RESULTS AND DISCUSSION

Table-1 shows the complexes together with colour, chemical analysis, melting/decomposition temperatures and magnetic moments. The analytical data show the formation of adducts.

TABLE -1
ANALYTICAL DATA, COLOUR, MELTING POINT AND MAGNETIC DATA OF
4-METHYL ACETOPHENONE *o*-HYDROXY-4'-BENZAMIDO THIOSEMICARBAZONE

S. No.	Complexes	Colour (m.p. °C)	% Analysis: Found (Calcd.) ⁴				μ_{eff} (B.M.)
			M	Cl	S	N	
1.	Co(C ₁₇ H ₁₈ N ₄ O ₂ S)(CH ₃ COO) ₂	Blue (290)	11.00 (11.35)	—	6.02 (6.16)	10.70 (10.79)	5.18
2.	Ni(C ₁₇ H ₁₈ N ₄ O ₂ S)(CH ₃ COO) ₂	Green (220 d)	11.10 (11.31)	—	6.08 (6.16)	10.71 (10.79)	3.08
3.	Cu(C ₁₇ H ₁₈ N ₄ O ₂ S)(CH ₃ COO) ₂	Brown (235 d)	12.04 (12.13)	—	6.05 (6.11)	10.62 (10.69)	1.60
4.	VO(C ₁₇ H ₁₈ N ₄ O ₂ S) ₂ SO ₄	Green (245 d)	5.95 (6.01)	—	11.21 (11.33)	13.16 (13.22)	1.82
5.	Co(C ₁₇ H ₁₈ N ₄ O ₂ S)Cl ₂ (H ₂ O) ₂	Blue (260 d)	11.52 (11.60)	13.90 (13.97)	6.22 (6.30)	10.98 (11.02)	4.90
6.	Ni(C ₁₇ H ₁₈ N ₄ O ₂ S)Cl ₂ (H ₂ O) ₂	Green (265 d)	11.50 (11.56)	13.92 (13.98)	6.21 (6.30)	10.97 (11.02)	3.20
7.	[Cu(C ₁₇ H ₁₈ N ₄ O ₂ S)Cl ₂ ·H ₂ O] ₂	Brown (250 d)	12.70 (12.84)	14.12 (14.35)	6.38 (6.47)	11.25 (11.32)	0.90

d—decomposed.

All the complexes are insoluble in water and common organic solvents but soluble in dimethyl formamide and dimethyl sulfoxide. The molar conductance

value of the complexes lie in the range 0.74–7.8 mhos $\text{cm}^2 \text{mol}^{-1}$ indicating their nonionic nature, while $\text{VO}(\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S})_2\text{SO}_4$ ($70.2 \text{ ohm}^{-1} \text{ cm}^2 \text{mol}^{-1}$) shows (1 : 1) ionic nature in solution⁶.

The magnetic moment of $\text{VO}(\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S})_2\text{SO}_4$ complex corresponds to one unpaired electron, irrespective of stereochemistry; it shows the presence of three absorption bands at 12500, 14280 and 21110 cm^{-1} . The last one is noticed as a shoulder on the main charge transfer band. The spectra of five coordinated oxovanadium(IV) systems are quite similar to those of the six coordinated systems and it is difficult to distinguish between the two geometries on the basis of observed electronic spectra^{7, 8}; however, as the chemical analysis and infrared spectra indicate, a five-coordinated structure for the complex is more probable and the three electronic spectral bands may be assigned as ${}^2\text{B}_2 \rightarrow {}^2\text{E}$ (12500); ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ (14280) and ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ (21110) cm^{-1} .

The electronic spectra of Co(II) complexes exhibit two bands in the regions 10600–8000 and 20100–18440 cm^{-1} which may be assigned to the transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ and ${}^4\text{T}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ respectively indicating octahedral stereochemistry around Co(II) in all the complexes⁹. Three bands are observed in both the Ni(II) complexes in the regions 10900–10180, 19080–15270 and 32600–26700 cm^{-1} , which are the characteristic of an octahedral symmetry around the Ni(II) ion¹⁰.

The subnormal- μ -effective values of $[\text{Cu}(\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S})\text{Cl}_2]\text{H}_2\text{O}$ and $[\text{Cu}(\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S})(\text{CH}_3\text{COO})_2]$ may be attributed to metal-metal or super exchange interaction¹¹ through bridging chloride and acetate respectively. Two bands are noticed at 15705 and 21070 cm^{-1} in the electronic spectrum of $[\text{Cu}(\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S})\text{Cl}_2]\text{H}_2\text{O}$ and at 16030 and 25020 cm^{-1} in that of $[\text{Cu}(\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S})(\text{CH}_3\text{COO})_2]$. The first one may be attributed to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}(\text{D})$ transition, presuming distorted octahedral geometry to the complex and the complex $[\text{Cu}(\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S})(\text{CH}_3\text{COO})_2]$ has square pyramidal geometry. The second band in both the complexes indicates dimeric nature of the complexes¹².

A comparison of infrared spectra (cm^{-1}) of the ligand with those of the complexes reveals the bonding mode of the thioamides to the Lewis acid. The $\nu(\text{C}=\text{S})$ mode appears at 930 cm^{-1} but gets shifted to 900 cm^{-1} in the spectra of all complexes except $[\text{Cu}(\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S})(\text{CH}_3\text{COO})_2]$ showing its involvement in chelation. The four ligand bands in the region 1500–1300 cm^{-1} (1470, 1420, 1380 and 1360 cm^{-1}) have been assigned to thioamide bands I and II, arising due to the coupled vibrations of $\delta(\text{NH})$, $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$. In the spectra of the complexes these bands shifted towards higher wavenumbers (1480, 1435, 1390 and 1380 cm^{-1} respectively). These shifts suggest the interaction of the thioamide group with metal ions.

Two broad bands at 1040, 930 and 820 cm^{-1} of the free ligand shifted towards lower wavenumbers (*ca.* 20 cm^{-1}) in the spectra of complexes. These bands have been assigned to thioamide bands III (having major contributions from $\nu(\text{C}-\text{C})$, $\nu(\text{C}-\text{N})$ and $\nu(\text{C}=\text{S})$ in the normal coordinate) and thioamide band IV primarily due to $\nu(\text{C}=\text{S})$ respectively. The shifts in the positions of these bands towards

lower wavenumbers in the complexes further confirmed the bonding of metal ion through thiocarbonyl sulphur.

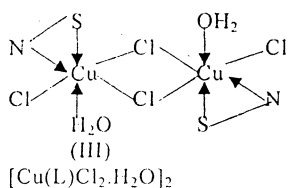
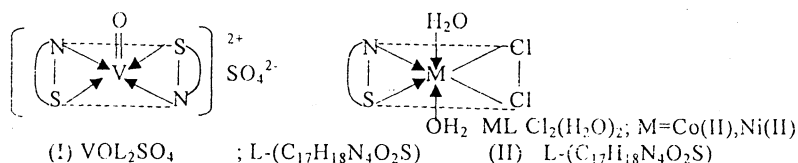
The ligands do not exhibit any band around 2500 cm^{-1} due to $\nu(\text{S—H})$ and this indicates the presence of thione form of the ligand in the solid state. The free ligand show a band around $1100\text{--}1090\text{ cm}^{-1}$ due to $\nu(\text{C=S})$ ^{13,14}. This band disappears in the IR-spectra of complexes and a new band in the range $680\text{--}660\text{ cm}^{-1}$ appears in the complexes due to $\nu(\text{C—S})$ mode¹⁵. Thus IR-data are indicative of sulphur coordination.

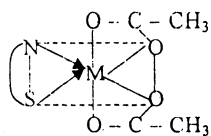
The ligands exhibit the $\nu(\text{C=N})$ in the region $1630\text{--}1605\text{ cm}^{-1}$ and this band shifts to lower energy side in complexes indicating nitrogen coordination¹⁶.

The IR-spectra of hydrated complexes exhibit bands in the regions $3410\text{--}3390$ and $900\text{--}880\text{ cm}^{-1}$ assignable to stretching and rocking modes of coordinated water molecule.

In $[\text{Cu}(\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S})(\text{CH}_3\text{COO})_2]$ only azomethine group frequency shifted to lower side whereas $>\text{C=S}$ is not disturbed, implying that only azomethine nitrogen is taking part in chelation. The positive shift in both $\nu_{\text{as}}(\text{O—C—O})$ (30 cm^{-1}) and $\nu_s(\text{O—C—O})$ 45 cm^{-1} in $[\text{Cu}(\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S})(\text{CH}_3\text{COO})_2]$ and a negative shift in $[\text{Co}(\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S})(\text{CH}_3\text{COO})_2]$ and $[\text{Ni}(\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S})(\text{CH}_3\text{COO})_2]$ with respect to the positions in sodium acetate indicate bridging bidentate behaviour¹⁷ in the former complex and chelating bidentate nature in the latter two complexes. The bands appearing as 1140 and 970 cm^{-1} in $[\text{VO}(\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S})_2\text{SO}_4]$ indicate ionic nature of sulphate ion. A strong band around 980 cm^{-1} in the infrared spectra of the solid signifies the presence of (V=O) group. The bands observed in the region $290\text{--}250\text{ cm}^{-1}$ are assigned to $\nu(\text{M—Cl})$ terminal vibrations¹⁸. The low intensity bands at 265 and 250 cm^{-1} are ascribed to $\nu(\text{M—Cl})$ bridging vibrations in case of Cu(II) complexes, in view of polymeric nature.

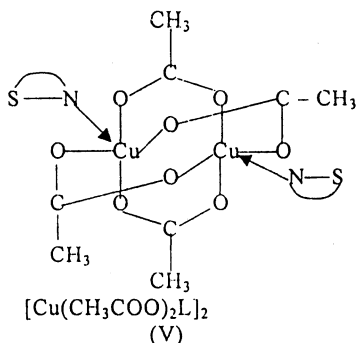
The non-ligand bands appearing at $325\text{--}290$ and $290\text{--}260\text{ cm}^{-1}$ in the spectra of complexes but absent in the spectra of ligand are tentatively assigned to $\nu(\text{M—N})$, and $\nu(\text{M—S})$ modes respectively¹⁹.





$ML(CH_3COO)_2$ M = Co(II), Ni(II)

L = $(C_{17}H_{18}N_4O_2S)$
(IV)



$[Cu(CH_3COO)_2L]_2$
(V)

Based on chemical analysis and physico-chemical methods, the following structures may be proposed.

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(Received: 16 May 2003; Accepted: 27 November 2003)

AJC-3247