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Studies on Coordination Behaviour of Co(II), Ni(II) and Cu(II) Complexes of Semicarbazones and Thiosemicarbazones

S. JHA* and R.P. VERMA

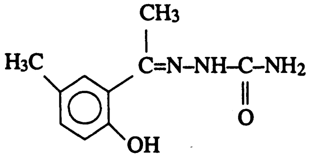
Department of Chemistry, Lalit Narayan Mithila University, Darbhanga-846 008, India

Co(II), Ni(II) and Cu(II) complexes of 2-hydroxy-5-methyl acetophenone/2-hydroxy-3,4-dimethoxy acetophenone semicarbazone, thiosemicarbazone and aminoguanidine have been prepared and characterized. Antimicrobial activities of the synthesized complexes have also been studied.

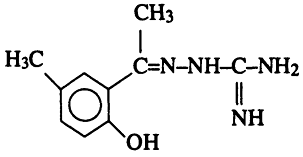
Key Words: Co(II), Ni(II), Cu(II), 2-Hydroxy-5-methyl acetophenone, 2-hydroxy-3,4-dimethoxy acetophenones, Semicarbazones, Thiosemicarbazones, Aminoguanidine.

INTRODUCTION

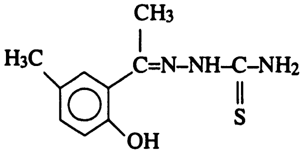
Semicarbazones and thiosemicarbazones have been used in medicinal chemistry, especially in the treatment of tuberculosis[1–4]. Antimicrobial and antitumour activity are also shown by thiosemicarbazones, semicarbazones and their metal complexes[5, 6]. In the present work, we report the preparation and characterization of metal complexes (Co^{2+}, Ni^{2+} Cu^{2+}) with semicarbazone, thiosemicarbazone and aminoguanidine derived from *o*-hydroxy acetophenone (Fig. 1).



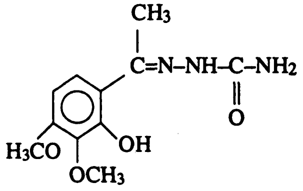
2-Hydroxy-5-methyl
acetophenone semicarbazone
(HMASZH$_2$)



2-Hydroxy-5-methyl
acetophenone amidoquadine
(HMAAGH$_2$)



2-Hydroxy-5-methyl
acetophenone semicarbazone
(HMATSZH$_2$)



2-Hydroxy-3,4-dimethoxy
acetophenone semicarbazone
(HDASZH$_2$)

EXPERIMENTAL

All the chemicals were of AR grade.

Preparation of Ligands: 2-hydroxy 5-methyl acetophenone or 2-hydroxy-3,4-dimethoxy acetophenone were dissolved in methanol (MeOH). Semicarbazide hydrochloride thiosemicarbazide hydrochloride and aminoguidine hydrochloride were dissolved in water. The solutions were mixed and refluxed for 30 min on a water bath. The reaction mixture was cooled, crystals were filtered, washed and recrystallized from alcohol.

Preparation of Complexes: A mixture of equimolar quantities (0.01 M) of the hydrated metal salts in distilled water and ligand solution in MeOH was refluxed for 2 h. The volume of the solution was reduced by evaporation and the resulting solids were washed with methyl alcohol (MeOH), dried and stored in a desiccator over $CaCl_2$[7].

The magnetic susceptibility data were obtained by Gouy method at room temperature. IR and electronic spectral data were obtained from CDRI, Lucknow.

RESULTS AND DISCUSSION

Studies of the ligands and their metal complexes was characterized by elemetal analysis, conductivity, magnetic moment measurements. IR and electronic spectral data are recorded in Table-1, whereas the electronic spectral data and magnetic data are presented in Table-2.

IR spectrum of semicarbazone complex showed the band at 1670–1660 cm^{-1} due to (C=O) stretching. In the spectra of the complex (C=O) stretching band is lowered by 10–30 cm^{-1} indicating the coordination through oxygen atom of keto form. A broad band observed around 3200 cm^{-1} in the free ligand is assigned OH (H-bonded). This bond disappears upon complexation indicating coordination through phenolic oxygen by deprotonation. The coordination through oxygen and nitrogen is further confirmed by the occurrence of new band at 460–425 cm^{-1} and 500-460 cm^{-1} respectively. A band observed at 3500–3400 cm^{-1} in the IR spectra of free ligand is assigned NH_2. This band remains unaffected upon complexation indicating non-involvement of NH_2 nitrogen in coordination.

IR spectrum of ligand complex with 2-hydroxy-5-methyl acetophenone aminoguanidine ($HMAAGH_2$) showed the (C=N) stretching frequency at around 1650-1600 cm^{-1}. This band is shifted to a lower value by about 10–25 cm^{-1} in all the complexes indicating the coordination of the imine group of Schiff base to the metal ion. The doublet band observed at 1700 cm^{-1} in the free ligand changes its position upon complexation. A broad band observed around 3200 cm^{-1} in the free ligand is assigned OH (H-bonded). This band disappears upon complexation indicating coordination through phenolic oxygen by deprotonation. A strong and sharp band in the range 500–490 cm^{-1} for Ni(II) complex and 470-460 cm^{-1} for Cu(II) complex was observed. This band is assigned to (M—N) (metal-ligand) stretching frequency.

IR spectra of complexes derived from thiosemicarbazones, *i.e.*, $HMATSH_2$ have been investigated. It has been shown that coordination takes place through nitrogen and sulphur in their complex. The coordination takes place through thio sulphur and azomethine sulphur in neutral medium[8].

TABLE-1
ANALYTICAL, PHYSICAL AND IR SPECTRAL DATA (cm^{-1}) FOR METAL COMPLEXES

Compound	ν(C=N)	ν(C=S)	Metal (%)	
			Found	Calculated
$Co[C_{10}H_{12}N_3O_2]Cl$	1580	—	19.52	19.61
$Co[C_{10}H_{13}N_4O]Cl$	1660	—	19.57	19.68
$Co[C_{11}H_{14}N_3O_4]Cl$	1585	—	19.89	17.01
$Co[C_{10}H_{12}N_3OS]Cl$	1610	1315	18.51	18.62
$Ni[C_{10}H_{12}N_3O_2]Cl$	1580	—	17.34	17.45
$Ni[C_{10}H_{11}N_3O_2]NH_3$	1570	—	20.81	20.80
$Ni[C_{10}H_{13}N_4O]Cl$	1610	—	17.36	17.50
$Ni[C_{10}H_{12}N_4O]NH_3$	1610	—	20.84	20.98
$Ni[C_{11}H_{14}N_3O_4]Cl$	1580	—	15.53	15.35
$Ni[C_{11}H_{13}N_3O_4]NH_3$	1570	—	17.84	17.96
$Ni[C_{10}H_{12}N_3OS]Cl$	1600	1140	16.54	16.66
$Ni[C_{10}H_{11}N_3OS]NH_3$	1615	1140	19.64	19.78
$Cu[C_{10}H_{12}N_3O_2]Cl$	1570	—	18.51	18.62
$Cu[C_{10}H_{11}N_3O_2]NH_3$	1565	—	21.91	22.08
$Cu[C_{10}H_1N_4O]Cl$	1625	—	18.54	18.67
$Cu[C_{10}H_{12}N_4O]NH_3$	1625	--	22.01	22.14
$Cu[C_{11}H_{14}N_3O_4]Cl$	1570	—	16.28	16.40
$Cu[C_{11}H_{13}N_3O_4]NH_3$	1565	—	19.01	19.15
$Cu[C_{10}H_{12}N_3OS]Cl$	1600	1140	17.64	17.78
$Cu[C_{10}H_{11}N_3OS]NH_3$	1610	1145	20.91	21.06

The ligand field spectra of Co(II) complexes Co·L·X having magnetic moment 4.90–5.10 B.M. showed three transitions ${}^4A_2 \xrightarrow{\nu_1} {}^4T_2(F)$ in the region 9500 (9910) cm^{-1}, ${}^4A_2 \xrightarrow{\nu_2} {}^4T_1(F)$ in the region 19000 (20000) cm^{-1} and ${}^4A_2 \xrightarrow{\nu_3} {}^4T_1(P)$ in the region 2200 (2300) cm^{-1} respectively. The magnetic moment value and elctronic spectral data are in good agreement with tetrahedral geometry[9, 10]. Hence Co(II) complexes are assigned tetrahedral geometry.

TABLE-2
ELECTRONIC SPECTRAL AND MAGNETIC SUSCEPTIBILITY DATA
OF METAL COMPLEXES

S.No.	Complex	μ_{eff} (B.M.)	Electronic spectra (cm^{-1})		
			ν_1	ν_2	ν_3
1.	[Co(HMASZH)Cl]	4.90	9500	19000	22000
2.	[Co(HMAAGH)Cl]	5.01	9600	19050	22150
3.	[Co(HDASZH)Cl]	5.05	9810	19500	22500
4.	[Co(HMATSZH)Cl]	5.10	9910	20000	23000
5.	[Ni(HMASZH)Cl·$2H_2O$]	2.95	10050	15000	25325
6.	[Ni(HMASZH)·NH_3]	Diamag.	15020	20140	25270
7.	[Ni(HMAAGH)Cl·$2H_2O$]	2.98	10100	15050	25380
8.	[Ni(HMAAG)·NH_3]	Diamag.	15250	20000	25300
9.	[Ni(HDASZH)Cl·$2H_2O$]	2.98	10150	15130	25400
10.	[Ni(HDASZH)·NH_3]	Diamag.	15000	20110	25000
11.	[Ni(HMATSZH)Cl·$2H_2O$]	3.05	10200	15140	25290
12.	[Ni(HMATSZ)·NH_3]	Diamag.	15060	20115	24740
13.	[Cu(HMASZH)Cl·$2H_2O$]	1.90	12050	—	—
14.	[Cu(HMASZ)·NH_3]	1.82	16130	—	—
15.	[Cu(HMAAGH)Cl·$2H_2O$]	1.91	12210	—	—
16.	[Cu(HMAAG)·NH_3]	1.80	16240	—	—
17.	[Cu(HDASZH)·Cl·$2H_2O$]	1.93	12610	—	—
18.	[Cu(HDASZH)·NH_3]	1.84	16350	—	—
19.	[Cu(HMATZSZH)Cl·$2H_2O$]	1.95	12700	—	—
20.	[Cu(HMATSZ)·NH_3]	1.85	16540	—	—

In reflectance spectra of Ni(II) complexes Ni·LH·$(H_2O)_2$ showed bands $^3A_{2g}\xrightarrow{\nu_1}{}^3T_{2g}$ in the region 10050 (10200) cm^{-1}, $^3A_{2g}\xrightarrow{\nu_2}{}^3T_{1g}(F)$ in the region 15000 (15140) cm^{-1}, $^3A_{2g}\xrightarrow{\nu_3}{}^3T_{2g}(P)$ in the region 25325 (25293) cm^{-1} respectively. These values indicate octahedral geometry around Ni(II) ion. This is further supported by magnetic moment values of 2.95 to 3.05 B.M. Ni(II) complexes Ni·L·NH_3 show three bands $^1A_{1g}\xrightarrow{\nu_1}{}^1A_{2g}$ at 5020 (15060) cm^{-1}, $^1A_{1g}\xrightarrow{\nu_2}{}^1B_{1g}$ at 20140 (20115) cm^{-1} and $^1A_{1g}\xrightarrow{\nu_3}E_g$ at 24740 (25270) cm^{-1}. These complexes show diamagnetic character. Diamagnetic complexes are normally of square-planar geometry. Diamagnetic is a consequence of eight elements being paired in the four lower lying *d*-orbitals[11].

The electronic spectra of Cu(II) complexes $Cu{\cdot}LH{\cdot}(H_2O)_2$ showed band at 12050 (12700) cm^{-1}, which may be assigned to the contribution of $^1B_{1g} \xrightarrow{\nu_1} {}^2A_{1g}$, $^2B_{2g}$ and ^2E_g. The magnetic moment values are 1.90–1.95 B.M. The band position and magnetic moment values are in a good agreement with for distorted octahedral geometry[14]. Cu(II) complexes $Cu{\cdot}L{\cdot}NH_3$ showed band width assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2A_{1g}$ and $^2E_{1g}$ at 16130 (16140) cm^{-1} with magnetic moments 1.82 to 1.85 B.M. respectively. This suggests square-planar geometry of the complexes[12].

Biological Activity: The antibacterial activity of the ligand 2-hydroxy-5-methyl acetophenone semicarbazone, 2-hydroxy-5-methyl acetophenone amidoguanidine, 2-hydroxy-3,4-dimethoxy acetophenone semicarbazone and their cobalt(II), nickel(II) and copper(II) complexes were determined by disc diffusion method (filter paper discs) against many microorganisms like *E. coli, S. typhi., V. cholerae* etc.[13, 14] Activity of semicarbazones, thiosemicarbazones and their complexes is more pronounced. Co(II) complexes exhibit stronger antimicrobial activity in comparison to ligands. Activity of amidoguanidines and their complexes could not be seen. Hence the ligands as well as complexes have significant importance for antitubercular, fungicidal and antitumour activities .

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Kinetics and Mechanism of the Oxidation of Adonitol by Hexacyanoferrate(III) Ion in Aqueous Alkaline Medium

N.F. QUADRI* and N.T. PATEL†

Department of Chemistry, Udaygiri College, Udgir, India

The rate of oxidation of adonitol by hexacyanoferrate(III) ion in aqueous alkaline medium is directly proportional to the organic substrate and hydroxide ion concentration. The rate of hexacyanoferrate(III) ion is first order at considered concentrations. A probable mechanism has been suggested.

Key Words: Kinetics and mechanism, Adonitol, Hexacyano-ferrate(III) Ion.

INTRODUCTION

The kinetics of oxidation of polyhydroxy alcohols have been less studied in alkaline medium. The data is available dealing with alkaline permanganate[1]. The kinetic data suggest that the oxidation involves the formation of a complex between the amount of substrate and $[Fe(CN)_6]^{2-}$. The complex gives the free radical and $[Fe(CN)_6]^{3-}$ ions.

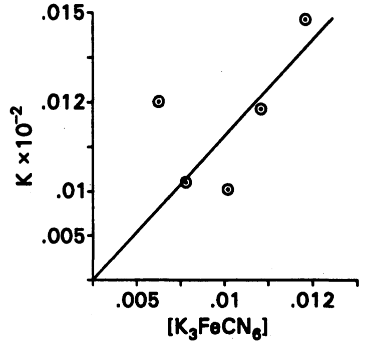
Oxidation kinetics of polyhydroxy alcohols has been studied by some workers[2–4].

RESULTS AND DISCUSSION

(a) Effect of variation of oxidant

At lower concentration of hexacyanoferrate(III) ion, the rate of reaction is found to be first order (Fig. 1). The concentration of hexacyanoferrate(III) varied for adonitol was 0.59×10^{-2} to 1.765×10^{-2} M.

The initial reaction rate values were calculated by plotting remainings of ferricyanide ion concentration against time.



Effect of variation of oxidant on rate of reaction
NaOH = 2.35×10^{-2} to 5.82×10^{-2} M.;
μ = 1 M at 30°C

Fig. 1

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†Department of Chemistry, Yashwant College, Nanded, India

TABLE-1

EFFECT OF VARIATION OF OXIDANT ON RATE OF REACTION

NaOH = 2.35 × 10^{-2} to 5.82 M × 10^{-2} (μ = 1 M at 30°C)

S.No.	$K_3[Fe(CN)_6]$	K × 10^{-2} (from graph)
1.	1.7646	1.260
2.	1.4700	1.134
3.	1.1760	1.100
4.	0.7350	1.090
5.	0.5900	1.005

(b) Effect of variation of susbstrate [Adonitol]

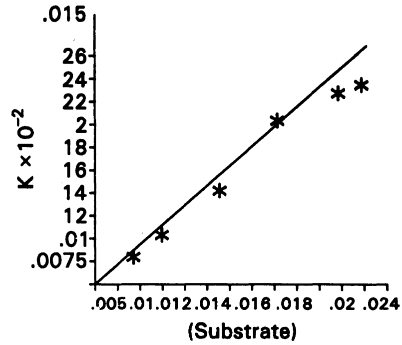
The substrate concentraion was varied from 2.35 × 10^{-2} M to 0.88 × 10^{-2} M. The rate of the reaction follows first-order kinetic, with respect to sodium hydroxide.

TABLE-2

EFFECT OF VARIATION OF ADONITOL ON RATE OF REACTION

NaOH = 2.35 × 10^{-2} to 5.82 M × 10^{-2} (μ = 1 M at 30°C)

S.No.	Adonitol × 10^{-2} M	K × 10^{-2} (from graph)
1.	0.88	0.860
2.	1.80	1.152
3.	1.47	1.450
4.	1.76	2.370
5.	2.05	2.370
6.	2.35	2.452

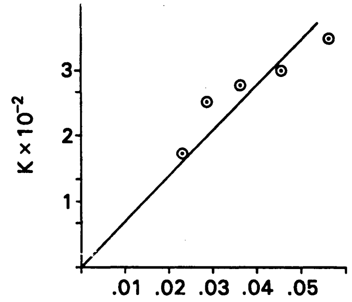


Effect of variation of adonitol on rate of reaction
NaOH = 2.35 × 10^{-2} to 5.82 × 10^{-2} M.;
μ = 1 M at 30°C

Fig. 2

(c) Effect of Variation of [NaOH] on the reaction rate

A graph between K_s values and [NaOH] gives a straight line passing through origin suggesting that order with respect to hydroxide ion is one. The concentration of NaOH is varied from 2.35 × 10^{-2} to 5.82 × 10^{-2} M.



Effect of variation of [NaOH] on rate of reaction
NaOH = 2.35 × 10^{-2} to 5.82 × 10^{-2} M.;
μ = 1 M at 30°C

Fig. 3

TABLE-3
EFFECT OF VARIATION OF [NaOH] ON RATE OF REACTION
NaOH = 2.35×10^{-2} to 5.82×10^{-2} M (μ = 1 M at 30°C)

S.No.	NaOH $\times 10^{-2}$ M	K $\times 10^{-2}$ (graphical)	K/NaOH
1.	2.35	1.84	0.7830
2.	2.90	2.86	0.9896
3.	3.52	2.94	0.8352
4.	4.05	3.17	0.7830
5.	5.80	3.84	0.6960

(d) Effect of variation of ionic strength on reaction rate

The ionic strength of the medium has been changed by using KCl at concentration of other reactants. The result indicates positive effect on ionic strength.

TABLE-4
EFFECT OF VARIATION OF IONIC STRENGTH
ON REACTION RATE
NaOH = 2.35×10^{-2} to 5.82 M $\times 10^{-2}$ (μ = 1 M at 30°C)

S.No.	KCl $\times 10^{-2}$	K $\times 10^{-2}$ M
1.	0.882	0.566
2.	1.764	6.200
3.	2.350	6.400

Mechanism

Taking the above observations in view at lower concentrations of reactants, the following rate expression may be suggested:

$$\frac{-d[Fey]}{dt} = [Fe(CN)_6]^{3-}[OH^{-}[s]] \qquad (I)$$

or

$$\text{Rate} = [Fe(CN)_6]^{3-}[OH]^1 \quad [\text{Adonitol}] \qquad (1)$$

where K is constant for adonitol. Literature reveals that the oxidation of organic substrate takes place both with $[Fe(CN)_6]^{3-}$ ion and $[Fe(CN)_6]^{2-}$ ion This is because when $[Fe(CN)_6]^{3-}$ ion is used as an oxidant in aqueous alkaline medium the following equilibrium exists:

$$3K^+ + [Fe(CN)_6]^{3-} \rightleftharpoons K_3[Fe(CN)_6]$$

It is also reported that the equilibrium[3] is also mainly towards right.

Thus, in order to explain the aforesaid results the reaction mechanism considering $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{2-}$ ion as oxidants is proposed in **Scheme-1**.

$$K^+ + [Fe(CN)_6]^{3-} \overset{K}{\rightleftharpoons} K[Fe(CN)_6]^{2-} \qquad \text{(I)}$$

$$S + OH^- \underset{K^{-1}}{\overset{K_1}{\rightleftharpoons}} S^- + H_2O \qquad \text{(II)}$$

$$S^- + [Fe(CN)_6]^{2-} \underset{\text{Slow}}{\overset{K_2}{\rightleftharpoons}} \text{Complex } (C_1) \qquad \text{(III)}$$

$$S^- + [Fe(CN)_6]^{3-} \xrightarrow[\text{Slow}]{K_2} \text{Complex } (C_2) \qquad \text{(IV)}$$

$$\text{Complex } (C_1) \xrightarrow[\text{Fast}]{K_4} S^\bullet + [Fe(CN)_6]^{3-} \qquad \text{(V)}$$

$$\text{Complex } (C_2) \xrightarrow[\text{Fast}]{K_5} S^\bullet + [Fe(CN)_6]^{4-} \qquad \text{(VI)}$$

$$S^\bullet + [Fe(CN)_6]^{2-} \xrightarrow{\text{Fast}} \text{Product} + [Fe(CN)_6]^{3-} \qquad \text{(VII)}$$

$$S^\bullet + [Fe(CN)_6]^{3-} \xrightarrow{\text{Fast}} \text{Product} + [Fe(CN)_6]^{3-} \qquad \text{(VIII)}$$

Scheme-1

The complexes formed in steps (III) and (IV) disproportionate at a faster rate as represented in steps (V) and (VI), but the oxidation rate would also depend on the concentration of the species of hexacyanoferrate(III) and (IV) and the rate of disappearance of hexacyanoferrate(III) ion concentration as

$$\frac{-d[Fey]}{dt} = K_2[s][KFe(CN)_6]^{2-} + K_3[s][KFe(CN)_6]^{3-} \qquad (2)$$

In order to derive the final rate law equation it would be most appropriate to assume the total hexacyanoferrate(III) ion concentration as

$$[Fe(CN)_6^{3-}]_T = [Fe(CN)_6]^{3-} + [KFe(CN)_6]^{2-} \qquad (3)$$

Thus considering the steady state condition and equation (3), the final rate law equation in terms of decreasing hexacyanoferrate(III) ion concentration would be given by equation (4).

$$\frac{-d[Fey]}{dt} = \frac{2K_1[s][OH][Fey]_T\{K_3 + K_2 + (KK^+)\}}{K_{-1}[1 + (KK^+)]] + [Fey]_T\{K_3 + K_2(KK^+)\}} \qquad (4)$$

The derived rate law equation (4) is almost consistent with the observed kinetics, *i.e.*, it shows first order kinetics with respect to substrate and hydroxide ion concentration as well as the retarding trend with respect to hexacyanoferrate(III) ion concentration. The final oxidation product is the corresponding acid.

EXPERIMENTAL

The standard solution of hexacyanoferrate(III) ion was prepared fom AR (BDH) sample Adonitol used of AR (BDH). Stock solution of NaOH (AR, BDH) was prepared in double distilled water. The ionic strength of the medium was followed by estimating the amount of hexacyanoferrate(II) ion produced after a definite time interval with a solution of ceric(IV) sulphate using ferroin as a redox indicator, The products were identified by TLC.

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