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Chelation Behaviour of Aceturic Acid with Co(II), Ni(II) and Cu(II)

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Aceturic acid consists of two parts *e.g.*, peptide part *i.e.*, CH_3CONH and -COOH part. It may act as bidentate ligand coordinating through either peptide or carboxylic acid part or both peptide as well as carboxylic acid part simultaneously forming chelates with transition metal ions. Some complexes of Co(II), Ni(II) and Cu(II) with aceturic acid have been prepared. The microanalysis and electrical conductivity of complexes revealed the formulation of complexes as ML_2X_2 where 'L' is aceturic acid and X' stands for α-picoline or pyridine. The comparison of infrared spectra of complexes with that of free ligand confirms the ligation point of the ligand through carboxylic acid and nitrogen of peptide part. Thus a 5-membered chelates are formed with Co(II), Ni(II) and Cu(II). The magnetic moment values of Co(II) complexes were found in the range of 4.90-4.93 BM at room temperature while it was in the range of 3.32-3.39 BM for Ni(II) complexes. Cu(II) complexes recorded magnetic moment 1.98-2.10 BM. These values are informative of octahedral symmetry around the metal ion which was confirmed by the electronic spectra of complexes.

Keywords: Aceturic acid, 5-Membered chelate, Metal(II) complexes.

INTRODUCTION

The interaction of metal ions with amino acids and small peptides in aqueous solvent provides simple models of metal protein interaction in enzymatic processes. Ambidentities in metal ion coordination with peptide bonds are well known[1]. Metal complexes with amino acids play important role in various biological systems. Transition metal ion chelates are exploited by industry in the large scale purification of α-amino acids and a wide range of drug and drug precursors containing an amino carboxylic acid moiety. Amino acids are important ligands in humans and other biosystems[2,3]. Their involvement in Cu(II) transport and metabolism is also well documented[4]. The amino acids are also useful in the prevention of damage to normal tissues including peripheral nerves during chemotherapy[5]. Amino acids like histadine has high degree of specificity for the H_2 receptor which reduces the acid and pepsin content as well as the volume of basal and stimulated gastric secretion. α-Amino acids are fundamental structural units of proteins which perform diverse biological functions such as regulation of metabolic processes, transportation of oxygen in body and catalyzing biological reactions[6]. Generally the reactivity of amino acids is modified when they are coordinated to metal ions and nature exploits this effect through the contraction of metal ion binding cavities within the active sites of many enzymes that serve to accelerate reactions which generally proceed too slowly to be useful in living system[7]. Keeping in view the potential chelating tendency of α-amino acids and their importance in biological and medicinal fields, we were motivated to undertake the present investigation of chelating behaviour of aceturic acid with Co(II), Ni(II) and Cu(II).

EXPERIMENTAL

All the chemicals used were of Anal-R grade. Glycine and acetic anhydride were procured from Aldrich and were used without further purification. α-amino acid and acetic anhydride were taken in equimolar ratio and mixed together. 2 mL of pyridine was added slowly to it and the whole solvent was heated on water bath with an air condenser. Yellowish solid of aceturic acid appeared which was filtered and washed with acetone. Finally, it was recrystallized in ethanol. The yield was about 77 % and m.p. was recorded 135 °C. This ligand was used for complexation with Co(II), Ni(II) and Cu(II). The complexes were prepared by the usual method of refluxing the metal salts and the ligand taken in 1:2 molar ratio for 2-3 h. The medium was made alkaline by the addition of a little of sodium acetate.

The content of carbon, hydrogen and nitrogen in complexes were determined by microanalysis on Perkin-Elmer 240 °C, H, N elemental analyzer. The estimation of Co(II) and Ni(II) in complexes was carried out in laboratory gravimetrically, while Cu(II) was estimated volumetrically using standard method. The IR spectra of the ligand and complexes were recorded on Perkin-Elmer 783 spectrophotometer as KBr pellets. Electrical conductivity of complexes were determined on conductivity meter CG 857 Schoot-Grate GmbH in DMF solvent of 10^{-3} M concentration with a deep type cell having pt electrode. The magnetic susceptibility of complexes was determined on Gouy-balance at room temperature using mercury(II) tetrathiocyanocobaltate(II) as calibrant. The electronic spectra of complexes were recorded on Perkin-Elmer Lambada 950 spectrophotometer in DMF.

RESULTS AND DISCUSSION

The percentage composition of aceturic acid and its complexes with Co(II), Ni(II) and Cu(II) with their molar conductivity has been displayed in Table-1.

The low values of electrical conductivity of complexes are indicative of their non-electrolytic nature[8,9]. The infrared spectra of complexes are very clumsy. However some important bands of interest are considered and explained here.

In peptide group of the ligand, there is a secondary amide group for which generally a strong band appears around 3300 cm^{-1} due to $\nu_{(N-H)}$ stretching vibration with a band at 1655 cm^{-1} due to $\nu_{C=O}$ of the amide group. This is called amide-1 band[10]. The other band appearing at 1550 cm^{-1} is mainly due to deformation vibration of -NH, *i.e.*, $\delta_{(N-H)}$ mixed with $\nu_{(C-N)}$ stretching vibration. This is called amide-II band. The amide-III band appears between 1360-1300 cm^{-1} mainly due to $\nu_{(C-N)}$ mixed with $\delta_{(N-H)}$. In the IR-spectra of metal complexes, the strong band appearing at 3300 cm^{-1} in the IR-spectra of free ligand due to $\nu_{(N-H)}$ shifts to lower frequencies and appears at 3270-3260 cm^{-1}. This is indicative of the coordination of nitrogen of peptide part of amino acid *i.e.*, aceturic acid to the metal ions in complexes[11,12]. The $\nu_{C=O}$ stretching frequency appearing at 1630 cm^{-1} undergoes bathochromic shift by about 20 cm^{-1} in the IR-spectra of complexes this confirms the coordination of nitrogen of peptide group of amino acid to metal ions[13]. The strong band appearing at 1660 cm^{-1} and a medium band appearing at 1420 cm^{-1} are safely assigned to $\nu_{asym}(COO^-)$. and $\nu_{sym}(COO^-)$, respectively of the free ligand. In the IR-spectra of complexes, the $\nu_{asym}(COO^-)$ gets decreased by 40-60 cm^{-1} and appears at 1620-1600 cm^{-1} in the IR spectra of complexes. However, the $\nu_{sym}(COO^-)$ absorption frequency undergoes bathochromic shift by 10-20 cm^{-1} in complexes and appears at 1440-1430 cm^{-1} in place of 1420 cm^{-1} in the free ligand spectra. It shows that COO^- group has taken part in coordination[14]. The $\Delta\nu (= \nu_{asym}-\nu_{sym})$ value is found to be 170-180 cm^{-1} if the difference in $\Delta\nu > 200$ cm^{-1}, COO^- group behaves as monodentate ligand coordinating through either of the two oxygens. Here, in the present case, the $\Delta\nu$ value is 170-180 cm^{-1} which confirms the monodentate nature of COO^- of aceturic acid to the metal ions[15,16]. The band appearing at 3550 cm^{-1} in the IR spectra of free ligand due to ν_{O-H} group was found missing in the IR spectra of complexes confirming the deprotonation of -OH of COOH group and coordination through deprotonated carboxylate anion[17]. The aforesaid mode of coordination of the ligand to the metal ions was further substantiated and confirmed by the appearance of two new bands in the far IR spectra of complexes. The band appearing at 560-532 cm^{-1} is fairly assigned to ν_{M-N} stretching vibration and the other appearing at 470-450 cm^{-1} was assigned to ν_{M-O} stretching vibration[18].

Thus, the comparison of IR spectra of complexes of Co(II), Ni(II) and Cu(II) with aceturic acid clearly indicates that the aceturic acid behaves as bidentate monoanionic coordinating through nitrogen of peptide part and oxygen of acid part. The important IR bands of complexes with their assignment are given in Table-2.

In addition to these bands, the IR spectra of complexes display some new bands which are not observed in the IR spectra of free ligand. A broad band appears at 3360-3350 cm^{-1} followed by a sharp band at 860-825 and 720-710 cm^{-1} in the IR spectra of complexes no. 1, 4 and 7. These bands may be assigned to stretching, rocking and wagging vibrations respectively of -OH group of coordinated water[19,20]. In the IR

TABLE- 1
% COMPOSITION OF LIGAND AND COMPLEXES. CALCULATED/(FOUND)

Compounds	Colour	M	C	H	N	λ_m (ohm^{-1} $cm^{-1}mol^{-1}$)
Ligand (aceturic acid)	Yellowish	-	41.03 (42.50)	6.00 (5.88)	12.00 (11.90)	-
$[Co(L)_2(H_2O)_2]$	Pinkish	18.01 (17.91)	29.36 (29.58)	4.90 (4.44)	8.56 (8.320)	8.00
$[Co(L)_2(Py)_2]$	Pink	13.12 (12.94)	48.11 (48.72)	4.90 (4.51)	12.47 (12.41)	7.72
$[Co(L)_2(\alpha\text{-pic})_2]$	Dull pink	12.35 (12.12)	50.32 (50.58)	5.45 (5.22)	11.70 (11.61)	7.65
$[Ni(L)_2(H_2O)_2]$	Light green	14.72 (14.41)	24.07 (24.62)	6.01 (15.96)	7.00 (6.90)	9.34
$[Ni(L)_2(Py)_2]$	Green	13.50 (13.34)	49.68 (49.89)	5.06 (4.94)	9.66 (9.50)	10.52
$[Ni(L)_2(\alpha\text{-pic})_2]$	Light green	12.31 (12.19)	50.34 (50.88)	5.45 (5.31)	11.75 (11.52)	10.34
$[Cu(L)_2(H_2O)_2]$	Green	19.16 (13.01)	28.95 (27.00)	08.00 (11.50)	08.00 (05.00)	12.56
$[Cu(L)_2(Py)_2]$	Green	14.46 (14.00)	49.14 (50.00)	05.00 (06.00)	9.55 (8.20)	11.34
$[Cu(L)_2(\alpha\text{-pic})_2]$	Bluish green	13.00 (12.50)	50.00 (49.80)	5.40 (4.50)	11.06 (11.00)	12.00

L = Aceturic acid (N-ethanoyl-2-aminoethanoic acid); Py = Pyridine, α-pic = α-picoline, (2-methyl pyridine)

TABLE-2

Sl. no.	Complexes	$\nu_{(N-H)}$	$\nu_{(C-O)}$	ν_{asvm} (COO^-)	ν_{svm} (COO^-)	$\nu_{(M-N)}$	$\nu_{(M-O)}$	$\nu_{(O-H)}$	$\delta_{(O-H)}$	$\nu_{aro.}$(C-H)	$\nu_{(CH_3)}$
1	$[Co(L)_2(H_2O)_2]$	3270	1650	1620	1440	560	470	3350	830	-	-
2	$[Co(L)_2(Py)_2]$	3275	1650	1615	1438	560	470	-	-	3070	-
3	$[Co(L)_2(\alpha\text{-pic})_2]$	3275	1650	1610	1435	560	470	-	-	320	2850
4	$[Ni(L)_2(H_2O)_2]$	3265	1648	1605	1433	545	465	3355	825	-	-
5	$[Ni(L)_2(py)_2]$	3270	1650	1605	1435	540	460	-	-	3070	-
6	$[Ni(L)_2(\alpha\text{-ico})]$	3270	1645	1600	1430	540	460	-	-	3020	2850
7	$[Cu(L)_2(H_2O)_2]$	3275	1645	1618	1440	530	450	3360	835	-	-
8	$[Cu(L)_2(Py)_2]$	3270	1650	1615	1438	535	450	-	-	3070	-
9	$[Cu(L)_2(\alpha\text{-pico})_2]$	3275	1650	1615	1435	535	455	-	-	3020	2850

spectra of complexes no. 2, 5 and 8, a medium band appears at 3070 cm^{-1} and a weak band at 1560 cm^{-1} which clearly shows the presence of the coordination of nitrogen of pyridine to metal ion in these complexes[21]. In complexes no. 3, 6 and 9, a sharp band appears 2850 cm^{-1} in addition to a sharp band at 3020 cm^{-1}. The first is assigned to ν_{aroC-H} stretching and the second to ν_{C-H} stretching of methyl group. They also display a band at 765 cm^{-1} due to ν_{C-N} vibration. The appearance of these bands is indicative of the presence of coordinated α-picoline in the coordination sphere of these complexes[22].

Magnetic and electronic spectra of complexes: The magnetic moment of complexes has been determined by Guoy balance method at room temperature. Cobalt(II) complexes record magnetic moment 4.90-4.93 BM. These values are higher than the values expected for 3 unpaired electrons (μ_s = 3.88 BM) in Co(II), a d^7 system, in weak O_h crystal field. The high values of μ of Co(II) O_h complexes may be attributed to appreciable orbital contribution from orbitally triply degenerate $^4T_{1g}$ crystal field component in O_h crystal field for the ground state term ^4F of d^7 system[8,9,23]. The electronic spectra of Co(II) complexes display three bands which may be assigned to the following transitions:-

$$\nu_1 = {}^4T_{2g} \leftarrow {}^4T_{1g} = 8200\text{-}8100\ cm^{-1}$$

$$\nu_2 = {}^4A_{2g} \leftarrow {}^4T_{1g} = 17990\text{-}17375\ cm^{-1}$$

$$\nu_3 = {}^4T_{1g}(P) \leftarrow {}^4T_{1g} = 29150\text{-}26310\ cm^{-1}$$

The values of different crystal field parameters were calculated on the basis of three electronic spectral bands and values have been tabulated in Table-3.

The values of various crystal field parameters are in good agreement with the reported values for O_h complexes of Co(II)[24,25]. The magnetic moment of Ni(II) complexes has been found 3.32-3.39 BM at room temp. Here the magnetic moment of Ni(II) complexes is greater that the spin only values corresponding to 2 unpaired electrons of d^8 system. Actually for the system having ground term A_{2g} there is no orbital contribution but the magnetic moment due to first order Zeeman effect[26] is given by:-

$$\mu_{eff.} = \mu_s(1\text{-}4\lambda/10Dq)$$

As λ is negative for Ni(II), d^8 system, μ_{eff} becomes greater than μ_s values, however the values are in good agreement for the reported values for O_h Ni(II) complexes[27]. The electronic spectra of Ni(II) complexes in the present study display three bands whose assignments are given to the following transitions:

$$\nu_1 = {}^3T_{2g} \leftarrow {}^3A_{2g} = 9420\text{-}9200\ cm^{-1}$$

$$\nu_2 = {}^3T_{1g}(F) \leftarrow {}^3A_{2g} = 15610\text{-}15160\ cm^{-1}$$

$$\nu_3 = {}^3T_{1g}(P) \leftarrow {}^3A_{2g} = 27425\text{-}26240\ cm^{-1}$$

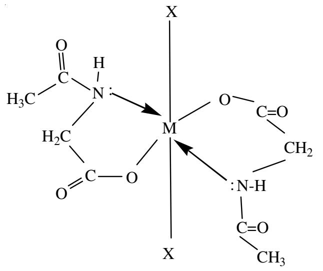
From these spectral data, the values of the different crystal field parameters which have been shown in Table-3. The values of various crystal field parameters are indicative of O_h geometry of Ni(II) complexes in the present study[28].

The magnetic moment of Cu(II) complexes falls in the range of 1.98-2.10 BM at room temperature which is in good agreement with the reported values for mononuclear O_h complexes of Cu(II)[29]. The electronic spectra of Cu(II) display one broad band which is assigned to spin allowed transition:

$$\nu_1 = {}^2T_{2g} \leftarrow {}^2E_g = 13250,\ 13320 \text{ and } 13410\ cm^{-1}$$

The band is equivalent to 10Dq. So, the values of 10Dq of Cu(II) complexes in the present study are 13320, 13250 and 13410 cm^{-1}, respectively. The broadness of the band may be attributed to the tetragonal distortion in their O_h geometry. The values of ν_1 and 10Dq are in good agreement with the values reported for distorted O_h complexes of Cu(II)[30].

The foregoing study of magnetic moment, electrical conductivity, IR spectra and electronic spectra of the complexes lead to structure of complexes as given below:



where, M = Co(II), Ni(II) and Cu(II) and X = H_2O, pyridine and α-picoline.

TABLE-3

S no.	Complexes	ν_2/ν_1	10 Dq	B	β_{35}	β (%)
1	$[Co(L)_2(H_2O)_2]$	2.142	9450	900	0.926	7.31
2	$[Co(L)_2(Py)_2]$	2.145	9270	927	0.954	4.53
3	$[Co(L)_2(\alpha\text{-pic})_2]$	2.142	9580	913	0.940	5.90
4	$[Ni(L)_2(H_2O)_2]$	1.667	9350	984	0.946	5.40
5	$[Ni(L)_2(Py)_2]$	1.647	9200	920	0.880	11.53
6	$[Ni(L)_2(\alpha\text{-pic})_2]$	1.657	9420	985	0.940	5.28

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