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SPECTRAL AND MAGNETIC STUDY OF SOME COMPLEXES OF N-FURFURYLIDINEACETAMIDE

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ABSTRACT
Complexes of Co(II) and Ni(II) with N-furfurylidineacetamide (NFA) are formulated as ML_2X_2 where M = Co(II) & Ni(II) while X_2 = Cl_2, Br_2 and I_2. The ligand is found to behave as neutral bidentate coordinating through azomethine nitrogen and endocyclic oxygen of furan ring to the metal ion forming a five membered chelate ring. The electrical conductivity data of complexes reveal their non electrolytic nature. The magnetic moment value of Co(II) complexes 4.92–5.00 BM which are much greater than μspin value i.e., 3.87 BM but slightly less than that expected from spin orbit coupling at room temperature. The μeff values of Ni(II) complexes are in the range of 3.04 t 3.14 BM. The three bands appearing in the electronic spectra of Co(II) complexes are assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions in octahedral crystal field. The crystal field parameters values of Co(II) complexes like 10Dq = 10,004–10321 cm^{-1}, B = 796.96–814.7 cm^{-1}. β_{35} = 0.82–0.83, β = 11–18% are indicative of slightly distorted octahedral geometry around Co (II) in these complexes. Ni(II) complexes displays five bands in their electronic spectra showing tetragonal distortion in their octahedral symmetry. The tetragonal distortion parameters Dt and Ds are found 308.5 to 422 cm^{-1} and 323to 454.5 cm^{-1} respectively. Thus the order of distorting capacity is found as I> Br> Cl.

KEYWORDS: N-furfurylidine acetamide, distorted Octahedral & Distorted tetragonalcomplexes.

INTRODUCTION
It is well known that many metal ions play an important role in biological system.[1,2] Metal ions are electron deficient, most biological macro molecules such as proteins and DNA etc are electron rich.[3,4] The attraction of these opposing charges leads to a general tendency for metal ions to bind to and to interact with biopolymers or another electron rich organic molecule. In coordination chemistry, especially involving the use of multidentate ligands, the nature of the metal bound chelate is critical in dictating the metal complex chemistry including structure, spin state, reactivity etc.[5-8] The ligand properties in question include the number of donor atoms, their identity, the overall ligand charge, overall ligand donor ability, steric interactions, and chelate size. In recent years the study of complexes containing N and O donor ligands has received great impetus attribute[9] to perhaps to their remarkable potential in inhibiting ribonucleotide reductase, an obligatory enzyme in DNA synthesis.[10,11] Consequently, compound containing these pharmacophores have been evaluated for their antiproliferative properties against a variety of tumors[12,13] O and N donor ligands of azodyes have also been used for complexation with transition metal ions[14] as they exhibit both chemotherpeutic and antiseptic properties.[15] Some azodyes are used for dying food stuffs, for preserving food grains and as redox indicator.[16-18] In continuation of our previous work,[19-22] herein we report the synthesis and spectral study of complexes of N-furfurylidine, an O & N donor ligand with Co(II) and Ni(II).

Experimental
All the reagents used were of Anal-R-grade. The ligand N-furfurylidine acetamide was prepared by the condensation of 2-furfural and acetamide in 1: 1 molar ratio.[23] The complexes were prepared by

refluxing the mixture of 5 m mole of metal salts (Co(II) & Ni(II) salts) and 10 m mole of the ligand i.e. N-furfurylidine acetamide in methanol for about three hours. On cooling the solution compounds appeared which were filtered and washed with methanol and then recrystallized from ethanol. They were dried on anhydrous $CaCl_2$. The yields were 75–80%.

RESULTS AND DISCUSSION

The results of micro analysis of the complexes are given in Table–1.

Table 1: Data of microanalysis of compound % cal/found.

S. N	Compounds	Colour	M	C	H	N	Cl	Br	I
1.	Ligand(NFA)	Dull Brown	–	61.31 62.00	5.14 5.28	10.21 10.02	–	–	–
2.	CoL_2Cl_2	Brown	(14.58) 14.39	(41.61) 41.80	(3.50 3.60	(6.93) 6.25	(17.54) 17.32	–	–
3.	CoL_2Br_2	Reddish Brown	(11.95) 11.21	(34.12) 34.35	(2.86) 2.92	(5.68) 5.32	–	(64.83) 61.61	–
4.	CoL_2I_2	Deep Brown	(10.03) 9.89	(28.65) 28.84	(2.40) 2.56	(4.47) 4.34	–	–	(43.24) 43.10
5.	NiL_2Cl_2	Orange	(14.54) 14.32	(41.63) 41.83	(3.50) 2.56	(6.93) 6.90	(17.55) 17.16	–	–
6.	NiL_2Br_2	Deep Orange	(11.91) 11.62	(34.12) 34.34	(2.86) 2.84	(5.68) 5.34	–	(32.43) 32.24	–
7.	NiL_2I_2	Light Orange	(10.00) 9.89	(28.66) 28.88	(2.40) 2.46	(4.77) 4.52	–	–	(43.25) 43.00

On the basis of which they were formulated as ML_2X_2 where M = Co(II) & Ni(II), L = N-furfurylidine acetamide and X = Cl, Br & I. The low conductance values (10.3–15.8) $ohm^{-1}cm^2mol^{-1}$) in DMF show the non electrolytic nature of these complexes as the molar conductance value of complexes in DMF solution fall in the range 85–100, 140–170 and 200–260 ohm^{-1} cm^2 mol^{-1} for 1 : 1, 2 : 1 and 3 : 1 electrolytes.[14,24] Out of the clumsy infrared bands displayed by the free ligand and complexes, some important bands and their assignments have been given in Table–2.

Table 2: Important FTIR Bands & Their Assignment (cm^{-1}).

S.N.	Compounds	νC=O	νCH=N	$\nu_{CH_3-\overset{\overset{O}{\|}}{C}-}$	νC–O–C
1.	Ligand (NFA)	1700	1630	1485	121
2.	CoL_2Cl_2	1700	1600	1480	1180
3.	CoL_2Br_2	1700	1605	1480	1180
4.	CoL_2I_2	1700	1600	1480	1175
5.	NiL_2Cl_2	1700	1595	1485	1775
6.	NiL_2Br_2	1695	1590	1480	1180
7.	NiL_2I_2	1690	~1590	1480	1170

The sharp band appearing at 1700 cm is assigned to the stretching vibration of C=O of the free ligand.[25-29] This band doesn't show any significant change in the FTIR spectra of the complexes. It shows the non involvement of carbonyl oxygen of the ligand in co-ordination. The sharp band at 1630 cm^{-1} displayed by free ligand is safely assigned to the stretching vibration of azomethine group (νCH=N) of the ligand.[30-32] This band suffers red shift by 25 to 35 cm^{-1} in the complexes which is indicative of coordination through azomethine nitrogen of the ligand.[30-32] The appearance of a weak band at 1600 cm^{-1} in the i.e. spectra of the free ligand is assigned to νC=C of the furan ring while the medium bands at 1365 cm^{-1} and 1280 cm^{-1} may be assigned to the deformation vibration of CH_3 and C–CH_3 stretching or –CH_3 rocking vibration respectively. In the FTIR spectrum of the free ligand a sharp band appears at 1210 cm^{-1} which is assigned to νC–O–C moiety of the furan ring of the free ligand. A significant decrease in this frequency by 30-35 cm^{-1} is observed in the spectra of the complexes which confirms the co-ordination to the metal ions.[33-38] The additional bands at 400-430 cm^{-1} and 500-520 cm^{-1} in spectra of complexes may be assigned to νM–N and νM–O vibration which further substantiate the co-ordination through azomethine nitrogen and endocyclic oxygen of the ligand. The appearance of new band at 200-300 cm^{-1} in the spectra of the complexes indicates the presence of halides in co-ordination sphere.[39-40]

Magnetic Moment and Electronic spectra

The magnetic moment values of Co (II) complexes fall in the range of 4.92 - 5.00 BM at room temperature. (Table–3)

Table 3: UV & Visible Bands and their Assignment (cm^{-1}).

S.N.	Compounds	ν_1	ν_2	ν_3	μ_{eff} (BM)
1.	CoL_2Cl_2	9100	18300	20100	4.92
2.	CoL_2Br_2	9000	18690	20000	4.98
3.	CoL_2I_2	8855	17800	19660	5.00

Assignment $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$, $^4A_{2g} \leftarrow {}^4T_{1g}(F)$, $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$

These values are higher than the μspin value (3.87 BM) for three unpaired electrons.

The ground state of Co(II), a d^7 system in octahedral field is $^4T_{1g}$ which is triply degenerate and hence orbital contribution is expected to the magnetic moment of Co(II) complexes. But the experimental values are slightly less than the full contribution of orbital moment. This may be due to slightly lowering of symmetry from O_h to O_{4h}. These values are in good agreement with the values reported for distorted octahedral complexes of Co(II).[41-43] Co(II) complexes display three bands in their electronic spectra. The bands with their assignment are given in Table–3. The first and the third bands are a bit more broad than the 2nd which is really very weak due to the involvement of two electrons transitions simultaneously. The various crystal field parameters have been derived[44] by the expression given below :

$\nu_3 - 2\nu_1 = 15B - 10Dq$.....(i)

$2212\nu 1 = 10Dq - 15B + [225\,B + 100Dq + 180Dq.B]2$...(ii)

$\nu_3 - 2\nu_1 = 15B - 10Dq$.....(iii)

The values of the different crystal field parameters for Co(II) complexes are given inTable–4.

Table 4

S.N.	Compounds	ν_2/ν_1	10 Dq cm^{-1}	B cm^{-1}	β_{35}	β
1.	CoL_2Cl_2	2.01	10,32	814.70	0.85	16%
2.	CoL_2Br_2	2.076	10,160	811.27	0.83	17%
3.	CoL_2I_2	2.010	10,000	796.96	0.82	18%

The ν_1 and ν_2 value, Dq value, β_{35} and B values correspond to almost octahedral symmetry around Co(II) ion with 16 to 18% covalency in these complexes.[30,32,43,45,46]

But the μeff values and the broadness ν_2/ν_3 bands are indicative of some distortion from perfect Octahedron symmetry. The magnetic moment values of Ni(II) complexes fall in the range of 3.04 to 3.14 BM. (Table–5).

Table 5: UV & Visible Bands and Their Assignment (cm^{-1}).

S.N.	Compounds	ν_1	ν_2	ν_3	ν_4	ν_5	μ_{eff} (BM)
1.	NiL_2Cl_2	8900	11600	15240	16790	27175	3014
2.	NiL_2Br_2	8420	11530	14100	16370	25910	3.04
3.	NiL_2I_2	8300	11490	13900	1610	25200	310
Assignment		$^3E_g{}^a \leftarrow {}^3B_{1g}$	$^3B_{2g} \leftarrow {}^3B_{1g}$	$^3A_{2g} \leftarrow {}^3B_{1g}$	$^3E_g{}^h \leftarrow {}^3B_{1g}$	$^3A_{2g}(P) \leftarrow {}^3B_{1g}$	

At room temperature which are in good agreement with the values reported for six co-ordinate.[25,26,46,47] These Ni(II) complexes display five bands in their electronic spectra. Which are given with their assignment in Table–5. One the basis of these bands, the calculation parameters, Racah parameters, Nephelauxetic effect have been derived as below:

$Dq_{(xy)} = 0.1\,(^3B_{2g} \leftarrow {}^3B_{1g})$ .....(i)

$Dq_{(z)} = 0.1\,(2\nu_1 - \nu_1)$ .....(ii)

D_t from equn. $Dq_{(z)} = 0.1(^3B_{2g} \leftarrow {}^3B_{1g}) - 1.75D_t$.....(iii)

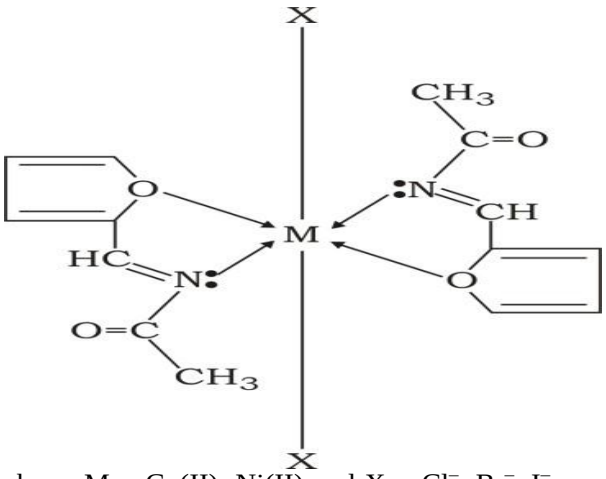
D_s from $6D_s = 0.1(\nu_4 - \nu_3) + 5/4\,D_t$ .....(iv)

The various parameters of Ni(II) complexes have been given in Table–6.

Table – 6

S.N.	Complexes	$Dq_{(xy)}$ (cm^{-1})	$Dq_{(z)}$ (cm^{-1})	D_t (cm^{-1})	D_s (cm^{-1})	B (cm^{-1})	β_{35}	β
1.	NiL_2Cl_2	1160	620	308.5	323	963	0.89	11%
2.	NiL_2Br_2	1153	631	355.4	451	896	0.83	17%
3.	NiL_2I_2	1149	411	422	454.5	797.8	0.74	26%

Thus all the three complexes of Ni(II) are octahedral with considerable tetragonal distortion and appreciable covalent character in M-L bands.[48-53] On the basis of D_t and D_s values the order of distortion capacity is given as : I > Br^- > Cl. The tentative structure of complexes may be given as.



where, M = Co(II), Ni(II) and X = Cl^-, Br^-, I^-

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