MICROWAVE ASSISTED SYNTHESIS AND STRUCTURAL CHARACTERISATION OF NICOTINIC ACID AND NITRITO−*KO* MIXED LIGAND COMPLEXES

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ABSTRACT

The mixed ligand complexes were prepared using nicotinic acid and nitrto-κO ions as ligands with Cr^{III}, Co^{II}, Ni^{II}, Cu^{II} and Cd^{II} ions. The complexes are identified as neutral, non electrolytes and distorted octahedral in structure for the Cr^{III}, Co^{II} and Ni^{II} complexes, tetragonal for the Cu^{II} and pseudo tetrahedral for the Cd^{II} complexes. These have been characterized by using elemental analysis, IR, magnetic susceptibility, conductance measurements and electronic spectral studies. The shifts of the ν(C=N) (azomethine) and ν (C=O) frequencies are monitored in order to find out the donor sites of the ligands. The nicotinic acid is neutral, monodentate and coordinates through the pyridine ring nitrogen. The elemental and spectral analyses interpret the geometry for these complexes.
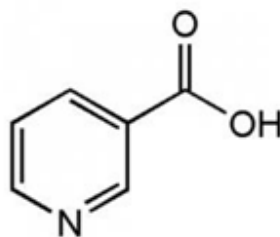
Keywords: Nicotinic acid Transition metal complexes, IR spectra, Electronic spectra.

INTRODUCTION

The synthesis and characterization of nicotinic acid ligands containing nitrogen donor site has extended great interest in recent times. Pyridine derivatives are associated with important biological activities such as fungicidal, antitumor and antibacterial etc. [1-4]. Nicotinic acid is found to be pharmacologically and physiologically active [5-9].
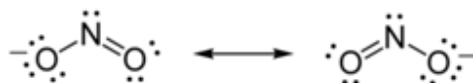
The present study is aimed at the preparation and structural elucidation of a few nicotinic acid (NAD) complexes by spectroscopic methods (UV and IR). In addition, a detailed analysis about the stereochemistry aspects of their metal complexes is obtained from spectral measurements. Comparisons of the IR spectrum of nicotinic acid with those of the metal complexes were useful in determining the atoms of the ligand that are coordinated with the metal ion. Magnetic and electronic spectral measurements have been done for the coloured complexes.

Nicotinic acid, also known as niacin, and though the two are identical in their vitamin functions, Nicotinic acid does not have the same pharmacologic and toxic effects of niacin, which occur incidental to niacin's conversion. Nicotinic acid acts as bidentate ligand whereas, the nicotinic acid exhibits monodentate behaviour, and both, having good ligating character, enhances the biological properties [10-13].

Nitrite is important in biochemistry as a source of the vasodilator nitric oxide. The nitrite ion is an ambidentate ligand and is known to bond to metal centres in at least five different ways. When donation is from nitrogen to a metal centre, the complex is known as a *nitrito -κN* complex. When donation is from one of the oxygen to a metal centre, the complex is known as a *nitrito- κO* complex. Both the oxygen atoms may donate to a metal centre, forming a chelate complex. A nitrite ion can form an unsymmetrical bridge between two metal centres, donating through nitrogen to one metal and oxygen to the other. A single oxygen atom can bridge two metal centres [14-18].

On the basis of the literature survey, no work has been done on coordination with nicotinic acid and nitrite ion. Metal nitrates for the complex preparation and their structures are analysed through UV-Vis, IR, magnetic susceptibility and electrical conductance measurements.

The metal complexes of Cr^{III}, Co^{II}, Ni^{II} Cu^{II} and Cd^{II} are prepared with nicotinic acid and nitrto–κO to assign their structure from the physiochemical studies.

MATERIALS AND METHODS

All the chemicals used for the preparation of the ligands were Alfa Aser quality, AR grade. Conductivity measurements ($\Omega^{-1}cm^{2}mole^{-1}$) were carried out in DMF using a Tacussel conductivity bridge model. Magnetic susceptibilities were determined using a Guoy balance at room temperature (25°C) with Hg [Co(SCN)$_4$] as standard. Pelkin-Elmer PE 938 spectrophotometers were used to record the IR spectra using KBr pellets. UV-visible spectra were recorded in acetone and chloroform on a Perkin-Elmer model 550-S spectrometer.

Preparation of the complexes
The complexes were prepared for the ligand nicotinic acid with counter anionic ligand nitrite. For the preparation of the complexes, the metal nitrates in methanol/ethanol were mixed with the organic and ionic ligands in the required mole ratios. The resulting mixture was irradiated in a microwave oven for about few minutes at medium power level (800W) with occasional shaking. The complexes obtained was cooled to room temperature, dried and kept in air tight

containers. Complexes were also synthesized by conventional method and results were found satisfactory.

RESULTS AND DISCUSSION

General properties

All complexes were coloured solids. The colours of the complexes are given in table1; they were in soluble in water. All are hygroscopic in nature at room temperature. Cr^{III}, Co^{II}, Ni^{II} and Cu^{II} complexes are coloured but the Cadmium complex is colourless. The colours of the complexes are given in Table1. All the complexes are soluble in dimethyl formamide. Some of them are soluble only in nitrobenzene and acetone.

Table 1 *Physical, analytical data of the complexes*

Complex	Colour	Mol. Wt.	M.P. (°C)	Yield (%)
$[Cr(NO_2)_3(NAD)_3]$	Brown	559	280	75
$[Co(NO_2)_2(NAD)_4]$	Pink	643	290	70
$[Ni(NO_2)_2(NAD)_4]$	Olive Green	642	290	60
$[Cu(NO_2)_2(NAD)_2]$	Blue	402	295	70
$[Cd(NO_2)_2(NAD)_2]$	Colourless	451	312	75

Analysis of the complexes

The percentage of metal present in the complexes was determined volumetrically. The results are given in table2. From the analytical data it is suggested that the ligand nicotinic acid acts as monodendate ligand.

Elemental Analysis, Magnetic moment, Molar Conductance of the complex

Complex	% M	% C	% H	% N	% O	$\mu_{eff.}$ BM.	Molar Cond. ($\Omega^{-1}cm^2mol^{-1}$)
$[Cr(NO_2)_3(NAD)_3]$	9. 30 (9.35)	38.64 (38.32)	2.95 (2.65)	15.01 (15.30)	34.60 (34.15)	3.17	18.25
$[Co(NO_2)_2(NAD)_4]$	9.15 (9.17)	44.50 (44.51)	3.41 (3.07)	13.10 (13.70)	43.44 (42.91)	5.92	17.15
$[Ni(NO_2)_2(NAD)_4]$	9.16 (9.18)	44.60 (44.41)	3.28 (3.12)	13.23 (13.74)	43.67 (42.86)	5.92	17.38
$[Cu(NO_2)_2(NAD)_2]$	15.78 (15.74)	35.85 (35.91)	2.72 (2.36)	13.96 (13.16)	32.96 (32.53)	4.90	19.89
$[Cd(NO_2)_2(NAD)_2]$	7.48 (7.43)	67.52 (67.54)	5.92 (5.89)	15.73 (15.75)	28.25 (28.21)	-	15.13

Conductance measurements

The molar conductances of the complex are analysed and are presented in table 3. The electrical conductivity of these complexes in

acetonitrile was measured. The molar conductance values obtained for these complexes at the concentration of 10^{-3} M are in the range of 10-20 ohm^{-1} mol^{-1} cm^2. These values are too low to account for any dissociation of the complexes in acetonitrile. Hence these complexes can be regarded as non-electrolytes and it is concluded that the nitrto-κO ions are covalently bonded to

Metal ions indicating that they act as ligands and not as simple ions [20]. Based on the analytical data and molar conductance measurements, the following compositions were assigned for the prepared complexes. $[Cr(NO_2)_3(NAD)_3]$ $[Co(NO_2)_2(NAD)_4]$ $[Ni(NO_2)_2(NAD)_4]$ $[Cu(NO_2)_2(NAD)_4]$ and $[Cd(NO_2)_2(NAD)_2]$ NAD→ Nicotinic acid NO_2 → nitrito-κO ion

Table2
Table 3. *Characteristic IR bands (cm^{-1}) of the ligand and its complexes*

Ligand / Complex	$\nu_{C=C}$	$\nu_{C=O}$	$\nu_{C=N}$	ν_{C-N}	ν_{M-N}	ν_{M-ONO}
Nicotinic acid	1532	1680	1612	1255		
$[Cr(NO_2)_3(NAD)_3]$	1537	1680	1560	1258	527	340
$[Co(NO_2)_2(NAD)_4]$	1534	1682	1594	1262	523	342
$[Ni(NO_2)_2(NAD)_4]$	1535	1682	1583	1267	529	346
$[Cu(NO_2)_2(NAD)_2]$	1533	1680	1610	1260	540	350
$[Cd(NO_2)_2(NAD)_2]$	1535	1684	1570	1272	535	342

Magnetic moments measurements
The Cr (III) complex showed a magnetic moment of 3.77 BM which is slightly lower than the spin only value of 3.87 BM expected for the three unpaired electrons.
The magnetic moment values for Cu (II), Co (II) and Ni (II) complexes are shown in Table 2. High spin Co(II) complexes usually have magnetic moment of 4.7-5.2 B.M and are lowered very much if the symmetry of ligand field departs from octahedral geometry. The magnetic moment of Co(II) complexes are in the range of 4.90 BM indicating that the Co (II) complexes are typically high spin complexes and having octahedral structure. High spin octahedral Ni(II) complexes usually have magnetic moment of 2.9-3.4 BM are lowered very much of the symmetry of the ligand field depart from octahedral geometry. The Ni (II) complexes exhibit the magnetic moment values in the range 3.8 BM, indicating octahedral co-ordination of the ligands around

Ni (II) ion. The Cu (II) complexes exhibit magnetic moment in the range of 2.11BM suggesting of distorted tetrahedral nature for these complexes [12].

Infrared spectral Analysis
The IR spectra of ligand with its octahedral complexes have been studied in order to characterise their structures. The IR spectra of the free ligand and its metal complexes were carried out in the 4000–200 cm^{-1} range. The IR spectra of all metal complexes were interpreted by comparing the spectra with those of the free ligand, and the results are listed in Table3. The relevant peaks alone are considered for discussion. The comparison of the band positions of various vibrations are ascertained with good evidence.

The presence of δ(COOH) asymmetric stretching vibration is confirmed by the band at

$1740 cm^{-1}$ and the symmetrical stretching vibration is observed at $1350 cm^{-1}$. In the infrared spectrum of metal complexes, the ν C=N stretching vibrations were observed at 1560-1610 cm^{-1} and were due to coordination of the nitrogen from C=N to the metal, stretching vibration for the nicotinic acid reduced at the complex. The uncoordinated nicotinic acid showed a strong peak at 1460 cm^{-1}, which is characteristic of the imine $\nu(C=N)$ group. The aromatic C=C that is directly attached with the pyridine nitrogen also affected upon complexation and are situated at a frequency significantly different than the free ligands. Coordination of the nicotinic acid ligand to the metal centre through the nitrogen atom is expected to reduce the electron density in the methine link and hence lower the $\nu(C=C)$ and $\nu(C=N)$ frequencies. The peak due to $\nu(C=C)$ is slightly shifted to lower frequencies and appears between 1576–1579 cm^{-1}, indicating the coordination of the imine nitrogen to the metal.

The peak at $1680 cm^{-1}$corresponds to the asymmetric C=O stretching confirms that all the complexes, the ligand do not coordinate with COOH oxygen. The free ligand showed a medium intensity band at 3210 cm^{-1} assigned to νCH vibrations, which has been observed in the 2820- 2850 cm^{-1} region in the case of the complexes. It can be observed that there is no considerable shift in the νCH vibrations in the case of the complexes compared to the ligands indicating non-involvement of acid group in the coordination. The low frequency skeletal vibrations due to M-N stretching provide direct evidence of the complexation and bands are observed in the 479-417 cm^{-1} region.[20,21]

Pyridine ring vibrations of free nicotinamide at 1592 cm^{-1} shifts to higher frequencies in the spectrum of the metal complexes. The shifts in the spectrum of the complexes may indicate that the pyridine ring is coordinated. The bands due to the asymmetric and symmetric stretching of carboxylate in the metal complexes occur in the range of 1679–1663 cm^{-1}. This shows that the coordination does not takes place through the carboxyl group [12]. The low intensity bands in the region of 456–400 cm^{-1} are attributed to M–N and M–O vibration [14, 15].

Electronic spectral Analysis

Electronic spectra of ligand L and their metal complexes in DMF solutions have been recorded in the 200 – 1100 nm range. The UV-Vis spectra of the ligand and metal complexes in DMF showed two to seven numbers of absorption bands between 268 and 734 nm. The bands below 455 nm are mostly associated with intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. In the electronic spectra of the ligand and their metal complexes, the presence of wide range of bands seems to be due to both the $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and d – d transitions of ligands and metals respectively and also due to charge transfer transition arising from π electron interactions between the metal and ligand that involves either a metal-to-ligand or ligand-to-metal electron transfer. The absorption bands observed within the range of 331–397 nm in DMF are mostly due to the transition of $n \rightarrow \pi^*$ of imine group corresponding to the ligand or metal complexes.

Cobalt (II) complexes

The electronic spectrum of the cobalt complexes exhibited three bands at 1567418832 and 25971 cm^{-1} that are assigned to the transitions $^4T_1g(F) \rightarrow {}^4T_2g(F)$ $^4T_1g(F) \rightarrow {}^4A_2g(F)$ and $^4T_1g(F) \rightarrow {}^4T_1g(P)$ respectively, suggesting an octahedral geometry around the Co(II) ion. The magnetic moments of Co (II) complexes were found to be 4.90 B.M. also indicating octahedral geometry. The Co(II) complex under the present investigation possess interelectronic repulsion parameter (B') 749 cm^{-1} is less than the free ion (B) value of $971 cm^{-1}$ suggesting

considerable orbital overlap and delocalization of electrons on the metal ion. The nephelauxetic ratio (β) for the Co (II) complex (0.778) is less than one, suggesting partial covalency in the metal ligand bond. The values Dq, β%, LFSE and υ_2/υ_1 (Table 4) suggest the distorted octahedral geometry for Co (II) complex.

Nickel(II) complexes

The absorption spectra of nickel (II) complexes display three d-d transition bands at 12108, 19416 and 27322 cm^{-1} are corresponds to $^3A_2g \rightarrow ^3T_2g$ $^3A_2g \rightarrow ^3T_1g(F)$ and $^3A_2g \rightarrow ^3T_1g(P)$. The magnetic moments of Ni (II) complexes were found to be 3.8 B.M supporting the d^8 high spin distorted octahedral structure.

The ligand field parameter such as Dq, B', β β% and LFSE have been calculated and the ratio υ_2/υ_1 was found to be 1.4046 which is well which the range (1.40-1.61) and is indicative of octahedral stereochemistry for this Ni (II) complex [28]. The Racha parameter B' is $852 cm^{-1}$, which is less than the free ion (B) value of 1040 cm^{-1} indicating the covalent character. The ratio υ_2/υ_1 and β% are also further supports the octahedral geometry around the Ni(II) ion These observations reveal that the nickel complexes possess an octahedral geometry and D_3 symmetry.

Copper(II) complexes

The magnetic moment values of Cu (II) complexes are 2.11 B.M. falls within the normal range observed for distorted octahedral complexes. In the present studies, all Cu (II) complexes each show, a single broad band in the range 18920 cm^{-1} due to transition between $^2Eg \rightarrow ^2T_2g$ suggesting tetragonal geometry. Tetragonal or square planar Cu (II) complexes are expected to give three bands. However, these three bands usually overlap in tetragonal complexes, to give one broad absorption band. The electronic spectra and magnetic moment data for all Cu (II) complexes coupled with the analytical, conductance data obtained for them, suggest the tetragonal geometry for the tetrahedral copper complex [29-32].

Ligand Field Parameters

Various ligand field parameters were calculated and their values are listed Table 4. The values of the ligand field parameters are consistent with octahedral geometry for the complexes. The ligand field strength, 10 Dq, can be estimated roughly for each complex by the relationship of nonlinear for all the anisotropic ligands.

Table 4 *Electronic spectral data and ligand field parameters of complexes*

Complex	υ_1	υ_2	υ_3	B'	β	β %	υ_2/υ_1	υ_3/υ_2	'λ'LFSE kcalmol^{-1}
[Cr(NO$_2$)$_3$(NAD)$_3$]	12345	18654	24378	949	0.80	20.00	1.5	1.3	37.43
[Co(NO$_2$)$_2$(NAD)$_4$]	11794	21978	25974	980	0.871	13.90	1.8	1.2	34.86
[Ni(NO$_2$)$_2$(NAD)$_4$]	13122	17932	-	865	0.796	21.10	1.4	-	35.56
[Cu(NO$_2$)$_2$(NAD)$_2$]	8892	15439	20085	749	0.778	23.03	1.7	2.1	27.17

The β values indicate the covalent character, which is due to the presence of σ and π bonds between the metal and ligands. Δ Values indicate the energy difference between the principle bands, which are formed due to ligand field absorption. This type of complex may have either C_4v or D_4h symmetry, which arises from the lifting of the degeneracy of the orbital triplet (in octahedral symmetry) in the order of increasing energy and assuming D_4h symmetry[13]. C_4v symmetry is ruled out because of the higher splitting of the first band. This suggests that it possesses distorted octahedral geometry around the metal ion [33, 34].

Powder X – ray Analysis

The XRD (Powder Pattern) of the complexes [Co(NO$_2$)$_2$(NAD)$_4$] and [Ni(NO$_2$)$_2$(NAD)$_4$] were indexed in X-ray diffractometer and the unit cell parameters have been calculated with the help of a computer from 2θ values (Fig. 3 and 4 respectively). The direct constant parameters like A, B, C, α, β, γ, V (volume) are given in Table 6. The density of the complexes has been determined by the floatation technique in a saturated solution of NaCl, KBr and benzene separately. The number of formula units per unit cell (n) was calculated from the relation

$$n = dNV/M,$$

Where, d = density of the compound, N = Avogadro's number, V = volume of the unit cell and M = Molecular weight of the complex.

The value of 'n' is found to be 10 for both complexes which agree well with the suggested monoclinic structure of the complexes. In addition, we have carried out powder X-ray diffraction studies of complex. Powder XRD pattern of [Co(NO$_2$)$_2$(NAD)$_4$]consists of 7 reflections in the range 5-50° (2θ) the inter planar spacing (d) has been calculated from the positions of intense peaks using Bragg's relationship. The 2θ values with maximum intensity of the peak for ligand was found to be 5.709 (2θ) which corresponds to d=15.4539. All the important peaks have been indexed and the observed values of inter planar distance were compared with the calculated ones.

It was found that there is good agreement between the calculated and observed values. The $(h^2+k^2+l^2)$ values are 1,5,27,32,58,72 and 74. The presence of forbidden number confirms the tetragonal systems. This implies that the Cobalt and Nickel Complexes are distorted octahedral in structure [35, 36].

Table 6 *X – Ray Powder Pattern Reports*

Compound	2 Θvalues			Unit Cell parameters	Density (gcc)	n	Possible geometry
	13.284	13.936	16.141				
	17.228	18.130	18.264	A=13.300 Å			
	19.300	21.756	22.659	B=20.543 Å			
	25.010	25.516	30.914	C=6.985 Å			
	32.051	39.253	41.659	α =90.000°			
	42.244	43.849	46.389	β=102.325°			
	47.308	48.194	49.881	γ =90.000°			
	50.032	51.419	53.174	V=1864.37			
[Co(NO$_2$)$_2$(NAD)$_4$]	53.541	53.976	54.076	Å^3	0.83	1	Monoclinic
	54.277	55.680	56.148				

56.265	56.466	56.766				
56.833	56.9S4	57.184				
57.836	58.0S7	58.621				
	13 066	13.417	14.804	.4=8.546 Å		
	21.856	22.241	23.761	B= 18.487 Å		
	26.084	27.956	32.668	C=7.371 Å		
	32.835	35.944	39.453	α =90.000°	1.25	1	Monoclinic
$[Ni(NO_2)_2(NAD)_4]$	41.458	44.216	46.422	β =1 06.893°		
	47.324	49.898	51.251	γ =90.000°		
	54.527	56.081	56.365	V=1114.34		
	59.306			Å³		

SUMMARY

The present study deals with the preparation and characterization of transition metal complexes of nicotinic acid and nitrite ion. Five complexes were prepared with Cr^{III}, Co^{II}, Ni^{II}, Cu^{II} and Cd^{II}. These structures are assigned on the basis of analytical, conductance, magnetic measurement, UV and IR spectral data.

     IR Spectra confirm the coordination of pyridine nitrogen of the nicotinic acid with the metal ion. The analytical data suggest that nicotinic acid acts as a monodendate ligand, and the complexes are in distorted octahedral geometry for the chromium, cobalt and nickel complexes and tetragonal for the copper and pseudo tetrahedral for the cadmium complexes. The conductance data suggests that the nitrite complexes are non ionic in nature and 1:0 electrolytes.

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L-87

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L-88