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Synthesis and Characterization of Nickel(II) Complexes with Azide Ion and Pyridine Derivatives as Ligands

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Nickel(II) complexes of the type $[Ni(N_3)_2(X)_3]_2$, where X = pyridine/2-picoline/3-picoline/4-picoline have been prepared and characterized on the basis of physico-chemical methods. The magnetic susceptibility data reveals that the complexes are high spin and six-coordinate with octahedral geometry. The spectroscopic data of these complexes show that they exist in the form of dimers with distorted octahedral structure. The analytical, magnetic moment and spectral data along with the geometry of nickel(II) complexes are discussed in the paper. The green coloured nickel(II) complexes correspond to the dimeric formulae: $[Ni(N_3)_2(py)_3]_2$, $[Ni(N_3)_2(2\text{-pic})_3]_2$, $[Ni(N_3)_2(3\text{-pic})_3]_2$ and $[Ni(N_3)_2(4\text{-pic})_3]_2$.

Key Words: Nickel(II) complexes, Azide ion, Pyridines.

INTRODUCTION

The role of nickel as an active oligo element was recently revealed[1]. The fact that chemotropic H_2-utilizing anerobic bacteria required nickel to grow and the subsequent identification of nickel as a component of hydrogenases provided definite proof of the biological role of nickel[2,3]. As nickel has the ability to bind hard and soft donor ligand, it leads to variety of geometries and oxidation states, with different reactivity in biological systems and in organometallic chemistry[4]. The chelation of ligands with transition metals is expected to form complexes with different structural geometry and may enhance their biological activity after chelation[5]. The substituents at the positions 2 (and 6) next to the donor atom such as pyridine and its derivatives, have a dramatic effect upon the stoichiometry and properties of the compounds formed[6].

EXPERIMENTAL

All chemicals used were of analytical reagent or equivalent grade. Pyridine, 2-picoline, 3-picoline and 4-picoline used were of E. Merck

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samples. The samples were distilled after drying with KOH pellets and used. Sodium azide (BDH) was used as such. The nickel complexes were prepared by the addition of excess of warm pyridine or picoline to the nickel(II) nitrate followed by the addition of a stoichiometric addition of 3 M aqueous sodium azide solution. The resulting solution was warmed on a water bath and allowed to stand for a 48 h crystallization. The nickel present in each complex was estimated by EDTA titration at suitable pH after decomposing a known weight of the complex with dilute mineral acid using murexide indicator[7]. The azide content in each azido complex was estimated by cerate oxidimetric titration[8] using ferroin indicator. Conductance measurements of the complex solutions (of the order of 10^{-3} M) in acetonitrile was carried out using a digital conductivity bridge (equiptronics digital conductivity meter EQ-660) with dip type standardized platinum cell. Magnetic susceptibilities of the complexes at room temperature were determined using Guoy balance (scientific equipments and services, Roorkee - EMU 75) with the field intensity of 11 K Gauss and a calibrated Guoy tube. The UV-Visible spectra of the complexes in the solid state (KBr medium) were obtained in the range of 220-800 nm by reflectance spectroscopic technique using a Hitachi U 3410 spectrophotometer. The vibrational spectra of the ligands in the complexes were recorded in the region 4000-400 cm^{-1} using the Shimadzu IR-435 spectrometer by dispersing them in the KBr disc (pellet technique). The far IR spectra of nickel-pyridine complex was recorded in the region 600-200 cm^{-1} using Bomem D 48 FTIR spectrometer by dispersing the sample in KBr. Thermogravimetric analysis was carried out using a thermogravimetric/differential thermal analyzer, Seiko Instruments Inc, Japan model 320.

RESULTS AND DISCUSSION

The complexes prepared were green coloured. Nickel and azide ion estimations correspond to the dimeric formulae of the complexes, *viz.*, $[Ni(N_3)_2(py)_3]_2$, $[Ni(N_3)_2(2\text{-pic})_3]_2$, $[Ni(N_3)_2(3\text{-pic})_3]_2$ and $[Ni(N_3)_2(4\text{-pic})_3]_2$ (Table-1).

The magnetic susceptibility values[9] for the nickel complexes indicate their paramagnetic character, corresponding to two unpaired electrons which confirming the +2 oxidation state of nickel. It is reported that the magnetic moments of octahedral nickel(II) complexes, in general lie in the range 2.9-3.3 BM. The observed magnetic data (Table-2) therefore reveals that the prepared complexes are with six-coordinate octahedral geometry.

The infrared spectrum of pyridine has the aromatic C-H stretching frequency at 3080-3010 cm^{-1}, C-N ring stretching frequency at 1600-1400 cm^{-1} and C-H out of plane bending frequency at 750-70 cm^{-1}. These

TABLE-1
ANALYTICAL DATA OF NICKEL(II) COMPLEXES

m.f.	Colour	Ni(II) (%)	N_3 (%)	Electrical Conductance* (ohm^{-1} cm^2 mol^{-1})
$[Ni(N_3)_2 (py)_3]_2$	Green	15.39 (15.44)	21.99 (22.11)	33.80
$[Ni(N_3)_2 (2\text{-pic})_3]_2$	Green	13.97 (13.91)	20.11 (19.91)	30.20
$[Ni(N_3)_2 (3\text{-pic})_3]_2$	Bluish green	14.15 (13.91)	19.73 (19.91)	37.20
$[Ni(N_3)_2 (4\text{-pic})_3]_2$	Bluish green	13.75 (13.91)	19.70 (19.91)	30.40

*30ºC in acetonitrile; Theoretical values are given in parentheses.

TABLE-2
MAGNETIC MOMENT, SPECTRAL DATA AND
GEOMETRY OF NICKEL(II) COMPLEXES

Complex	μ_{eff} (BM)	Electronic spectra		IR spectra N_3^- SSF (cm^{-1})	Probable geometry
		Δ_{max} (nm)	Assignments		
All nickel complexes	–	~310	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$ (obscured by CT)	–	DO
$[Ni(N_3)_2 (py)_3]_2$	3.10	632.3	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	1300	DO
$[Ni(N_3)_2(2\text{-pic})_3]_2$	2.78	657.9	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	1310	DO
$[Ni(N_3)_2(3\text{-pic})_3]_2$	3.16	613.3	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	1300	DO
$[Ni(N_3)_2(4\text{-pic})_3]_2$	2.79	617.9	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	1280	DO

SSF-Symmetric stretching frequency; DO-Distorted octahedral

frequencies are present in the respective regions in all the complexes prepared. This is in accordance with the report that in the frequency region above 650 cm^{-1}, the pyridine vibrations show very little shift upon the complex formation[10]. The symmetric stretching frequency[11,12] of the azide ion, 1344 cm^{-1} was shifted to the lower frequency region by 30-60 cm^{-1} and the asymmetric stretching frequency of the azide ion, 2040 cm^{-1} was found at about 2000 cm^{-1} for each complex. The above observations indicate the entry of azide ion into the coordination sphere of the nickel complexes (Table-2).

It is reported that in the case of azide, the deformation frequency[13,14] of N-N-N is observed at 645 cm^{-1}. On complexation, this frequency is shifted by 70-100 cm^{-1} to lower frequency values[12]. In addition, a metal-azide nitrogen stretching frequency is observed in the region 450-300 cm^{-1}. Pyridine shows as in-plane deformation frequency[15] at 604 cm^{-1} and an out-of-plane deformation frequency at 405 cm^{-1}. In the complex spectrum[16] they are shifted to a high frequency region by 20-40 cm^{-1}. The deformation of N-N-N and the out of plane deformation frequency in pyridine for $[Ni(N_3)_2(py)_3]_2$ were found at 296 and 431 cm^{-1} respectively.

The six coordinate complexes are generally high spin[9] and these complexes have absorption bands in the frequency ranges of 8000-13000, 15000-19000 and 25000-29000 cm^{-1} corresponding to the transitions $^3T_{1g}(P)$, $^3T_{1g}(F)$, $^3T_{2g} \leftarrow {}^3A_{2g}$, respectively. The $^3T_{1g} \leftarrow {}^3A_{2g}$ band is obscured by the CT band and the $^3T_{2g} \leftarrow {}^3A_{2g}$ band, which is expected in the range of 770-1250 nm, could not be observed as the spectrum was recorded in the wavelength of 200-800 nm[17]. The $^3T_{1g} \leftarrow {}^3A_{2g}$ band was observed (Table-2) in the visible region for each of the complexes.

The thermogram of $[Ni(N_3)_2(py)_3]_2$ indicates the removal of 15 mg of solvent from 100 mg of the complex from 32 to 40°C. The weight loss of 33.6 mg from 40 to 125°C corresponds to the loss of 2 mol of azide and 2 mol of pyridine. The thermogram of $[Ni(N_3)_2(3\text{-pic})_3]_2$ shows the degradation (12.4 %) at its first stage from 29.7 to 79°C with a removal of 1 mol of nitrogen and 1 mol of 3-picoline from the complex. The second stage involves 30.5 % removal of 2.5 mol of nitrogen and 2 mol of 3-picoline from 79.4 to 110°C. The third and last stages at 110 to 160°C and 320°C involve the removal of 11 and 28.7% (1 mol of 3-picoline and 2 mol of nitrogen and 3-picoline) and leaving 2 g atoms of nickel with 1 mol of nitrogen (Tables 3 and 4).

Hence on the basis of analytical, magnetic moment, IR, Far-IR, UV-Visible and TGA data, the Ni(II) complexes have the stoichiometry of the type $[Ni(N_3)_2(X)_3]_2$ which can be presumed to have a distorted octahedral geometry.

TABLE-3
TGA DATA FOR $[Ni(N_3)_2(py)_3]_2$ COMPLEX

Type of degradation	Temperature at which degradation		Degradation (%)	Possible species evolved
	Starts (°C)	Ends (°C)		
Minor	32.0	40.0	15.0	Solvent molecules
Major	40.0	125.0	33.6	2 mol of azide and 2 mol of pyridine

TABLE-4
TGA DATA FOR [Ni$(N_3)_2$(3-pic)$_3$]$_2$ COMPLEX

Type of degradation	Temperature at which degradation		Degradation (%)	Possible species evolved
	Starts (ºC)	Ends (ºC)		
Minor	29.7	79.4	12.4	1 g atom of nitrogen and 1 mol of 3-picoline
Major	79.4	110.0	30.5	2.5 mol of nitrogen and 2 mol of 3-picoline
Minor	110.0	160.0	11.0	1 mol of 3-picoline
Major	160.0	320.0	28.7	2 mol of nitrogen and 2 mol of 3-picoline

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