

Studies in Some Nickel(II) Complexes

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Adduct of bis oxine nickel with pyridine, β - and γ -picoline have been prepared. Nickel(II) complexes of the above bases with nitrate, glycollate and lactate as anion have also been isolated. The compounds have been analysed and structures have been suggested on the basis of magnetic and spectral studies.

Complex formation between pyridine and substituted derivatives have been studied widely¹⁻³ and compounds with composition $[ML_4]^{++}$ and $[ML_6]^{++}$ have been reported⁴. Hexacoordinating tendency has been shown in various tertiary base adducts of nickel complexes^{3,5}. In the present investigation adduct formation of pyridine, β - and γ -picoline with nickel oxinate has been attempted in non-aqueous solvent. Isolation of complexes of pyridine and its derivatives with nickel has also been attempted in aqueous solution with nitrate, glycollate and lactate as the anions.

EXPERIMENTAL

1. *Preparation of the adducts*: To the mixture of nickel chloride and pyridine (or β - or γ -picoline) in nearly 1 : 2 ratio with little excess of base, an alcoholic solution of 8-hydroxyquinoline was added. The mixture was allowed to stand over night. Yellowish-brown crystals settled down.

The solids were filtered out and washed with alcohol impregnated with corresponding base ($\sim 5\%$), dried in vacuum desiccator and analysed (Table 1). The analysis corresponds to composition $[Ni(\text{oxine})_2L_2] \cdot 2H_2O$. The compounds were heated at 110° in an oven and the resulting yellow compounds were also analysed in each case. The analysis (Table 1), indicates that the composition is $[Ni(\text{oxine})_2] \cdot 2H_2O$.

2. *Preparation of nickel glycollate and lactate*: Nickel lactate and nickel glycollate were prepared by refluxing nickel carbonate (in excess) with lactic and glycollic acid. The filtrate was evaporated to dryness and recrystallised. Their analyses corresponding to $[NiX_2]$ ($X =$ glycollate or lactate ion) and visible spectra in aqueous solution resembling that of $[Ni(H_2O)_6]^{++}$ indicate that they are simple salts.

3. *Preparation of nickel complexes*: Concentrated equimolar aqueous solutions of nickel salts (nickel nitrate, nickel glycollate and nickel lactate) and tertiary bases were mixed in 1 : 2 ratio with slight excess of the ligand, pH being maintained at ~ 6 .

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Partial precipitation of nickel hydroxide took place. Solution was filtered and refluxed for about 3 hrs. Solution was concentrated and evaporated under reduced pressure till blue crystals were obtained. The solid was washed with ether several times to remove excess ligand and dried. Solids could be isolated in case of pyridine, β - and γ -picoline but only $\text{Ni}(\text{OH})_2$ was precipitated in case of α -picoline. The analyses are given in Table 1.

TABLE 1

Analytical data and other properties of the complexes

Compound	Colour	Calc. %		Found %		B.M.	λ_{max} ($m\mu$)
		Ni	N	Ni	N		
1. $[\text{Ni}(\text{oxine})_2(\text{py})_2] \cdot 2\text{H}_2\text{O}$	Yellowish green	10.84	10.35	10.72	10.12	3.2	$\sim 540 \sim 830 \sim 950$
2. $[\text{Ni}(\text{oxine})_2(\beta\text{-pic})_2] \cdot 2\text{H}_2\text{O}$	Greenish yellow	10.31	9.84	10.40	9.63	3.1	$\sim 540 \sim 830 \sim 950$
3. $[\text{Ni}(\text{oxine})_2(\gamma\text{-pic})_2] \cdot 2\text{H}_2\text{O}$	Brownish yellow	10.31	9.84	10.45	9.71	3.1	$\sim 540 \sim 830 \sim 950$
4. $[\text{Ni}(\text{oxine})_2] \cdot 2\text{H}_2\text{O}$	Yellow	15.32	7.33	15.10	7.16	—	
5. $[\text{Ni}(\text{py})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$	Blue	15.58	14.86	15.62	15.25	3.12	$\sim 640 \sim 950$
6. $[\text{Ni}(\beta\text{-pic})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$	Blue	14.50	13.83	14.42	12.95	3.19	$\sim 640 \sim 950$
7. $[\text{Ni}(\gamma\text{-pic})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$	Blue	14.50	13.83	14.89	14.50	(absorbs) water	$\sim 640 \sim 950$
8. $[\text{Ni}(\text{py})_2(\text{H}_2\text{O})_2](\text{gly})_2$	Blue	14.57	6.95	14.10	6.17	2.87	$\sim 650 \sim 960$
9. $[\text{Ni}(\beta\text{-pic})_2(\text{H}_2\text{O})_2](\text{gly})_2$	Blue	13.62	6.50	13.06	6.84	2.72	$\sim 650 \sim 960$
10. $[\text{Ni}(\gamma\text{-pic})_2(\text{H}_2\text{O})_2](\text{gly})_2$	Blue	13.62	6.50	13.02	5.94	(absorbs) water	$\sim 650 \sim 960$
11. $[\text{Ni}(\text{py})_2(\text{H}_2\text{O})_2](\text{lact})_2$	Blue	13.62	6.50	12.96	5.93	2.94	$\sim 650 \sim 960$
12. $[\text{Ni}(\beta\text{-pic})_2(\text{H}_2\text{O})_2](\text{lact})_2$	Blue	12.79	6.10	12.87	5.96	2.76	$\sim 650 \sim 960$
13. $[\text{Ni}(\gamma\text{-pic})_2(\text{H}_2\text{O})_2](\text{lact})_2$	Blue	12.79	6.10	12.69	6.15	2.93	$\sim 650 \sim 960$

gly = $\text{CH}_2\text{OHCOO}^-$ and lact = $\text{CH}_3\text{CHOHCOO}^-$

In presence of excess ligand and at higher pH values mainly the hydroxide of nickel was isolated, although a small amount of the above mentioned complexes was isolated from the filtrate.

Magnetic studies: Magnetic susceptibilities of all the compounds were determined at room temperature using Gouy method⁶ and were found as shown in Table 1.

Spectral studies : The absorption spectra of the complexes were determined in the range 400–1000 $m\mu$ using Spectromom 360 (Hungarian) spectrophotometer. The spectra of the oxine adducts, were recorded in a mixed solvent system of alcohol and the corresponding base in 4 : 1 ratio. In case of tertiary base complexes with nitrate, glycollate and lactate as anions, solutions were prepared in water. The bands in the absorption spectra have been shown in Table 1.

In case of latter compounds, I.R. Spectra were also obtained in the form of pellets with KBr.

DISCUSSION

The above observations clearly indicate that adducts of nickel oxinate with pyridine, β -picoline and γ -picoline molecules are formed. That the resulting compounds are adducts, is indicated by the fact that no compound is obtained with α -picoline, which may be explained to be due to the steric hindrance. The weak linkage of the tertiary bases is indicated by their low thermal stability. At about 110°, the yellow-brown compounds turn yellow indicating that the tertiary bases are lost resulting in the formation of nickel oxinate. The water of crystallisation appear to be held strongly and this may presumably be due to strong hydrogen bonding involving oxine molecules. The experimental evidences are not adequate to substantiate the explanation. The compounds are unstable in aqueous medium and a yellow solid, $[\text{Ni}(\text{oxine})_2] \cdot 2\text{H}_2\text{O}$, has been isolated by treating the adduct with water. The displacement is evidently due to dilution effect.

The solutions of adducts (0.01M) in 1 : 3 pyridine (or β - or γ -picoline) and alcohol mixture (of negligible conductance) are found to be almost nonconducting (molar conductance ~ 1.5 mhos) indicating that they are nonelectrolytes.

The observed magnetic moment values (~ 3.2 B.M.) for the adducts are suggestive of an octahedral stereochemistry for the present Ni(II) complexes. Spin-orbit coupling due to higher state mixing may be responsible for somewhat higher values of B.

The visible absorption spectra of the adducts show three peaks at ~ 540 , ~ 830 and ~ 950 $m\mu$ corresponding to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ transitions⁸. Distortion, due to the coordination of oxygen and nitrogen of oxine, is insignificant because of almost similar field strength of the atoms. The peak position in the spectra of the three complexes do not differ much because of similar binding tendencies of the bases as shown by their formation constants in solution⁹.

In case of the other set of studies, the analysis of the compounds corresponds to the composition $[\text{NiL}_2(\text{H}_2\text{O})_2]\text{X}_2$ (where L = pyridine, β - or γ -picoline and X = nitrate, lactate or glycollate). Presence of glycollate and lactate in the outer sphere is indicated by the fact that compounds are freely soluble in water.

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The magnetic moment values of the complexes with nitrate, glycollate and lactate are almost same, indicating that glycollate and lactate also behave as nitrate and exist in outer sphere. The values of magnetic moment ~ 2.9 B.M. is in agreement with spin only value¹⁰ of two unpaired electrons and indicates the presence of polymeric octahedral or tetrahedral structure in solid state¹¹.

The visible absorption spectra show the presence of peaks at ~ 650 and ~ 960 $m\mu$. The peak positions being different from $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, it is indicated that the complex ions are stable in aqueous solution. The nature of the peak is same in all the cases indicating that nitrate, glycollate and lactate behave alike. The low intensity of the peaks ($\epsilon = \sim 4.0$) is suggestive of distorted octahedral structure (due to the coordination of solvent molecules) rather than tetrahedral structure.

I.R. Spectra of the compounds show the characteristic bands of the pyridine ring and hydroxy acids. Bands in the region $1600\text{--}1300$ cm^{-1} are attributed to the ring stretching vibration and represent interaction of $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretching vibration. Bands appearing in the region $1200\text{--}1000$ cm^{-1} are due to C-H in plane deformation. In case of nitrates, bands are observed at ~ 1380 and ~ 821 cm^{-1} corresponding to stretching and banding modes. In case of the complexes with glycollate and lactate ions in the outer sphere additional bands are observed in $1300\text{--}1200$ cm^{-1} region corresponding to O-H bending frequency and additional bands at ~ 950 cm^{-1} probably corresponding to C-O deformation. In all compounds the band at ~ 515 cm^{-1} corresponds to M-N stretching frequency. The band at ~ 640 cm^{-1} corresponds to M-O stretching and confirms the presence of coordinated water.

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