CHAPTER VII

QUATERNARY COMPLEXES OF Ni(II), THIOACIDS, CATECHOL AND TERTIARY AMINES.

Excellent coordinating ability, and ready availability, have made pyridine and its derivatives one of the most studied classes of ligands. Since the nitrogen atom is incorporated into a conjugated π system, there is the possibility of back donation of non-bonding metal d electrons into vacant acceptor antibonding $p\pi$ orbitals of the pyridine ring. Although the extent of π bonding in most metal-pyridine bond is not considered to be great, many properties of pyridine complexes are best accounted for, in terms of some back donation.

Thioglycollic acid and thiolactic acid are known to form number of complexes with number of metal ions,[1-6] catechol is also reported to form number of complexes with number of metal ions.[7-11] Pyridine is also known to form adduct[12] of type $Ni(L)_2X_2$ where L = bidentate ligand and X = pyridine. Mixed complexes of type $[Zn.A.L.]X.H_2O$ where A = dipyridyl or o-phenanthroline and L = thioglycollic acid or thiolactic acid have been reported by Panchal and Bhattacharya.[13] Mixed complexes containing polyphenols and dipyridyl (Chapter IV) or ethylenediamine[10,11] have also been isolated. An attempt was therefore, made to prepare the mixed ligand complexes of the type $[Ni.A.L.]^{2-}$ where A = catechol, L = thioglycollic or thiolactic acid. They could not, however, be isolated as such, instead the quaternary adducts $[MALX_2]Na_2$ were obtained in solid state.

Experimental and Discussion :

To 25 ml. of 0.5M nickel chloride solution was added

25 ml. of 0.5M thioacid solution. No precipitation was observed. The pH of the solution was raised by NaOH till there was formation of $[\mathrm{Ni(thio\ acid)(OH)_2}]\mathrm{Na_2}$ complex. This was then filtered and was dissolved in concentrated aqueous solution of catechol. Part of the complex was dissolved. The solution was filtered. To the filtrate was added a requisite quantity of pyridine or β- or γ-picoline till greenish blue complex was obtained. The complex was filtered and washed with water impregnated with corresponding tertiary base, and finally washed with ether. It was dried and analysed for nickel, nitrogen, sulphur and sodium contents. The results are presented in the following table.

Table

Complex	% Found	% Required
1. $[\mathrm{NiTGACat.(py)_2}]\mathrm{Na_2.2H_2O}$	Ni = 12.30	Ni = 12.60
	N = 5.26	N = 5.66
	S = 5.81	S = 6.10
	Na = 9.90	Na = 9.95
2. $[\mathrm{NiTGACat.(\beta\text{-}pic)_2}]\mathrm{Na_2.2H_2O}$	Ni = 11.90	Ni = 12.11
	N = 4.76	N = 5.20
	S = 6.10	S = 6.42
	Na = 8.90	Na = 9.31
3. $[\mathrm{NiTGACat.(\gamma\text{-}pic)_2}]\mathrm{Na_2.2H_2O}$	Ni = 12.00	Ni = 12.11
	N = 4.84	N = 5.20
	S = 6.31	S = 6.42
	Na = 8.85	Na = 9.31
4. $[\mathrm{NiTLACat.(py)_2}]\mathrm{Na_2}$	Ni = 12.10	Ni = 12.42
	N = 5.64	N = 5.82
	S = 7.93	S = 8.52
	Na = 8.83	Na = 9.71

5. $\left[\text{NiTLACat.}(\beta\text{-pic})_2\right]\text{Na}_2$	Ni = 11.81 N = 5.14 S = 5.62 Na = 8.90	Ni = 12.01 N = 5.49 S = 6.36 Na = 9.15
6. $\left[\text{NiTLACat.}(\gamma\text{-pic})_2\right]\text{Na}_2$	Ni = 11.93 N = 4.93 S = 5.92 Na = 8.65	Ni = 12.01 N = 5.49 S = 6.36 Na = 9.15

Conductance Measurements :

The compounds are insoluble in water and also in organic solvents and hence it was not possible to determine the conductance.

Magnetic Studies :

For the actual measurements of the magnetic susceptibilities, Gouy's method, as detailed earlier was followed. Complexes were found to be diamagnetic. The magnetic moment measurement was repeated at 60°C.. The temperature was attained in a rather crude way by dipping the capillary tube in water at 60°C.. The compound was found to be paramagnetic. The exact value have not been determined because the temperature falls down during weighing.

Reflectance Spectra :

Reflectance spectra were obtained in the region 400 - 1000 mμ.. Broad peak is obtained at 680 mμ and a less intense peak at 840 mμ.. The nature of the spectra corresponds to distorted octahedral complex.[14]

I.R. Spectral Studies :

The I.R. spectra of the compounds were obtained in the KBr phase. Bands obtained are as follows :

Compound	Characteristic bands cm^{-1}
1. $[\mathrm{NiTGACat.(py)_2}]\mathrm{Na_2.2H_2O}$	~ 3600(w), ~ 3200(w), ~ 1600(m), ~ 1500(m), ~ 1450(w), ~ 1400(w), ~ 1300(w), ~ 1220(w), ~ 1160(w), ~ 1080(m), ~ 1060(m), ~ 910(w), ~ 860(w), ~ 820(w), ~ 780(w), ~ 750(s), ~ 700(m), ~ 640(w), ~ 600(w), ~ 570(w), ~ 440(w), ~ 400(w).
2. $[\mathrm{NiTGACat.(\beta\text{-}pic)_2}]\mathrm{Na_2.2H_2O}$	~ 3450(w), ~ 3050(w), ~ 1600(w), ~ 1490(m), ~ 1400(w), ~ 1280(m), ~ 1200(m), ~ 1130(w), ~ 1110(w), ~ 1070(w), ~ 1050(w), ~ 880(m), ~ 800(s), ~ 775(m), ~ 760(s), ~ 720(w), ~ 650(m), ~ 600(w), ~ 575(w), ~ 500(w), ~ 425(w).
3. $[\mathrm{NiTGACat.(\gamma\text{-}pic)_2}]\mathrm{Na_2.2H_2O}$	~ 3400(w), ~ 3200(w) ~ 2500(w), ~ 1600(w), ~ 1500(w), ~ 1400(w), ~ 1270(w), ~ 1250(w), ~ 1220(w), ~ 1080(w), ~ 1040(m), ~ 900(w), ~ 810(s), ~ 789(w), ~ 760(m), ~ 550(w), ~ 500(s), ~ 425(w).
4. $[\mathrm{NiTLACat.(py)_2}]\mathrm{Na_2}$	~ 3600(w), ~ 3300(w), ~ 3120(w), ~ 3070(w), ~ 2500(w), ~ 1800(w), ~ 1610(m), ~ 1500(m), ~ 1460(s), ~ 1280(m), ~ 1220(m), ~ 1160(m), ~ 1100(s), ~ 1080(s), ~ 1050(s), ~ 920(w), ~ 860(m), ~ 770(m), ~ 750(s), ~ 700(m), ~ 640(w), ~ 575(w), ~ 470(w), ~ 460(w), ~ 425(w).
5. $[\mathrm{NiTLACat.(\beta\text{-}pic)_2}]\mathrm{Na_2}$	~ 3080(w), ~ 2800(w), ~ 2600(w), ~ 1600(w), ~ 1500(m), ~ 1380(w), ~ 1280(m), ~ 1200(m), ~ 1150(w),

		~1070(m), ~ 1040(m), ~ 1000(w), ~ 875(s), ~ 800(s), ~ 750(s), ~710(s), ~ 660(w), ~ 600(m), ~ 550(w), ~ 500(w), ~ 425(w).
6.	$[NiTLACat.(\gamma\text{-pic})_2]Na_2$	~ 3200(w), ~ 3080(w), ~ 2800(w), ~ 1800(w), ~ 1630(w), ~ 1590(w), ~ 1500(m), ~ 1450(w), ~ 1280(s), ~ 1210(m), ~ 1110(m), ~ 1080(w), ~ 1050(s), ~ 1000(w), ~ 920(w), ~ 870(s), ~ 810(s), ~ 750(s), ~ 730(m), ~ 600(w), ~ 500(m), ~ 425(w), ~ 400(w).

Discussion :

The above observations show that the complexes correspond to 1:1:1:2:2 ratios with respect to Ni(II), TGA or TLA, catechol, pyridine, or β- or γ-picoline and sodium.

The complexes were found to be diamagnetic indicating that the complexes are of square planar type, bidentate thio acids and catechol molecules occupying four positions. However, the compounds have two tertiary base molecules in the structure. Though addition of pyridine, or β- or γ-picoline results in the precipitation of the compound, similar reaction is not observed in case of α-picoline. This shows that the tertiary base molecules are not in the outer sphere. They must be occupying 5th and 6th positions in the inner sphere around the metal ion. α-picoline with $-CH_3$ group at α-position feels steric hinderance and hence, adduct formation cannot take place. Such observations has been made in ternary systems earlier.[15] The octahedral complexes of Ni(II) should have exhibited paramagnetism corresponding to two unpaired electrons.

Such cases of diamagnetism in octahedral complex of Ni(II) have been observed earlier.[16] It can be considered that the tertiary base molecules are loosely held along Z axis. The field along Z axis is, therefore, much less than along XY plane. Consequently energy separation between $d_{x^2-y^2}$ and d_{z^2} orbital is significant. The electrons get paired in the lower d_{z^2} orbital rather than being singly occupied in d_{z^2} and $d_{x^2-y^2}$. Such diamagnetic complexes should exhibit paramagnetic character on heating because of the depairing of electrons in d_{z^2} orbital and their promotion to higher energy $d_{x^2-y^2}$ orbital.[16] This is the reason why the compounds are found to be paramagnetic at higher temperature.

Reflectance spectra fig. VII 1 shows broad peak at 680 mμ. and a less intense peak at 840 mμ.. The nature of the spectra corresponds to distorted octahedral structure.[14]

I.R. spectra of the complexes exhibit bands corresponding to catechol, thio acids and tertiary amines. The TGA complexes with two water molecules show broad hydrogen bonded -OH band in the region 3600-3200 cm^{-1}. Band at 3080 cm^{-1} corresponds to C-H stretching frequency. In the case of free mercapto acids, a band is expected at 2550 cm^{-1} corresponding to S-H frequency. This band is absent in the spectrum of all complexes indicating that H-atom of S-H group gets dissociated as a result of coordination of sulphur with Ni^{2+} ion. The bands at nearly 1600-1580 cm^{-1} correspond to COO^- group stretching frequency. There is not much change in the value of COO^- stretching frequency from free ligand value. This indicates that the covalent interaction between metal and carboxylate group is less and the band is more of electrostatic type. Bands at 1600-1400 cm^{-1} correspond to catechol and pyridine ring stretching modes. The bands at nearly 1400 cm^{-1} and nearly 1250 cm^{-1} correspond to deformation and wagging of $-CH_2$ group. The C-C stretching band occurs in the region nearly 1200-1000 cm^{-1}. Bands obtained in the region 900-750 cm^{-1} correspond to ring and C-H out of plane deformation. The band at 720 cm^{-1} corresponds to C-S stretching vibration. The two lowest frequency bands of pyridine 605 cm^{-1} and 405 cm^{-1} suffer significant shifts to higher frequency upon complex formation.[17] In case of our quaternary complexes the bands at 640 and 450 cm^{-1} may be due to corresponding pyridine bands. The bands at 400 cm^{-1} and 425 cm^{-1} correspond to M-O (Metal-Catechol) stretching and M-S stretching, respectively. Due to weak interaction between metal and tertiary base M-N frequency may occur at lower frequency and could not be obtained.

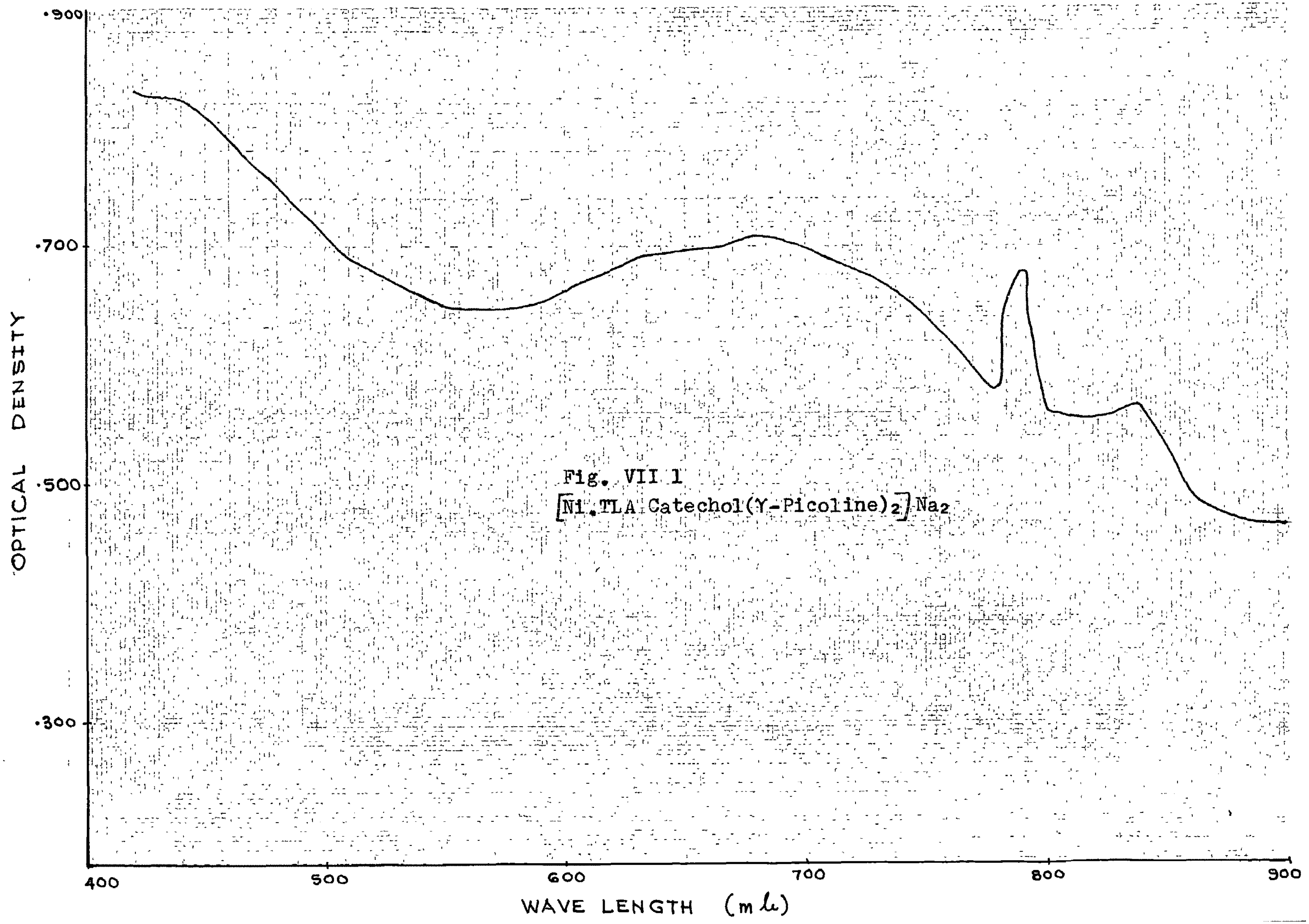

Fig. VII 1

$[\text{Ni.TLA Catechol(Y-Picoline)}_2]\text{Na}_2$

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