

The above data agreed in all respects with the reported data for (I) in literature. The direct comparison with the natural sample could not be made due to the non-availability of the sample.

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### STEREOCHEMICAL FEATURES OF SOME Ni(II) COMPLEXES OF 2-AMINO-PYRIDINE : THIOSEMICARBAZIDE AND ITS SUBSTITUTED THIOSEMICARBAZONE

In the present work, Ni(II)-complexes of 2-amino-pyridine : thiosemicarbazide (APT) and its substituted thiosemicarbazone, viz., 1-benzilidine, 4-( $\alpha$ -pyridyl) thiosemicarbazone (BPT) and 1-ortho hydroxy benzilidine, 4-( $\alpha$ -pyridyl) thio-semicarbazone (HO-BPT) have been prepared and characterized. Various ligand field parameters have been evaluated using Konig's approach<sup>1-3</sup>. The ligands were prepared by reported methods<sup>4</sup> and recrystallised from ethanol.

[Ni(APT)<sub>2</sub>Cl<sub>2</sub>]: Ni(II) chloride hexa hydrate (10 m mole) in 40 ml ethanol was mixed with the ligand-APT (20 m mole) in the same solvent. The reaction mixture was refluxed for ~ 2 hrs at low temperature and then set aside in a petridish, to evaporate at room temperature, for several days. The light brown crystals obtained were thoroughly rinsed with ethanol-acetone mixture and then dried under vacuum at room temperature. Yield ~ 65% [Found: Ni, 12.19; C, 30.22; H, 3.52; N, 24.47; S, 13.28; Cl, 15.51. Calcd. for [Ni(C<sub>6</sub>H<sub>8</sub>N<sub>4</sub>S)<sub>2</sub>Cl<sub>2</sub>] Ni, 12.66; C, 30.90; H, 3.43; N, 24.03; S, 13.73; Cl, 15.23%].

[Ni(APT)<sub>2</sub>(CN)<sub>2</sub>] and [Ni(APT)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]: The above procedure was repeated followed by the addition of KCN and NH<sub>3</sub> solutions to obtain greyish white and greyish brown substances respectively and the crystals dried *in vacuo*.

[Ni(APT)<sub>2</sub>(OH)<sub>2</sub>]: Ethanolic solution of Ni(II) nitrate hexa hydrate (10 m mole) with ligand-APT (20 m mole) in the same solvent was mixed, a dark bluish green solution was obtained (pH = 4.5), from which brown coloured chelate was obtained by adding aq. NaOH upto pH 6.5 and dried completely under vacuum.

[Ni(BPT)<sub>2</sub>]Cl<sub>2</sub>: On mixing acetonic solution of Ni(II) chloride hexa hydrate (10 m mole) and ligand BPT (20 m mole) a yellowish green coloured solution was obtained (pH 4.5), which on refluxing (~ 2 hrs) at low temp. (60-70° C) and successive concentration

under vacuum afforded brown coloured crystals of the complex.

[Ni(HO-BPT)Cl<sub>2</sub>.H<sub>2</sub>O]: A yellowish green coloured reaction mixture was obtained when acetonic Nickel(II) chloride hexa hydrate (10 m mole) was mixed with the ligand HO-BPT (10 m mole) in the same solvent. Shining green coloured complex was obtained on refluxing and concentrating at low temperature (60-70° C).

All compounds gave satisfactory C, H and N analyses.

The molar conductance measurements of 10<sup>-3</sup> M solutions of the complexes in DMF reveal that complex [Ni(BPT)<sub>2</sub>]Cl<sub>2</sub> is univalent electrolyte and the other complexes are non-electrolytes. The magnetic moment values lie in the range 2.91-3.50 BM which are well within the range (2.8-3.2 BM) expected for octahedral geometry.

The electronic spectra of the complexes were recorded as reported earlier<sup>5</sup>. The calculated values of the transitions  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  and the value of the Racah parameter have been evaluated according to the reported methods. The inner configurational transition ( $\beta$ ) and LFSE depend significantly on the method adopted for their calculation (Table I). The values of  $\beta$  of these complexes are between 0.5 and 1.0, clearly indicate the partial covalent character of the bond concerned. It has also been concluded that the best results may be obtained by the method which results from fitting the some of second and third bands.

In the infrared region, the ligand display characteristic absorption bands attributable to (NH) stretching at 3250-3175 cm<sup>-1</sup>. The (NH) bending modes in the region 1560 cm<sup>-1</sup> are obscured by modes associated with pyridine ring system of the ligand. Secondly, no characteristic changes were observed in the frequencies at 1640 and 1610 cm<sup>-1</sup> in APT-complexes (attributed to  $\delta$  (NH<sub>2</sub>) and amide band) and this implies non-participation of hydrazide nitrogen in coordination. In the complexes of BPT and HO-BPT, bands due to imine nitrogen  $\nu$  (C=N) are shifted towards lower frequencies and sharp peaks are generally reduced to shoulders, suggesting involvement of imino-nitrogen in coordination. It has been observed that the symmetric and antisymmetric  $\nu$  (C=C) +  $\nu$  (C=N) vibrations of pyridine ring either weakens or in some cases a slight upward shift (10-30 cm<sup>-1</sup>) occur on coordination, suggesting metal-pyridine bonding in complexes. The bands at 1333-1308 and 1136 cm<sup>-1</sup> (APT), 1266 and 1156 cm<sup>-1</sup> (BPT) and 1274 and 1190 cm<sup>-1</sup> (HO-BPT) are shifted to higher wave numbers while the bands 760 cm<sup>-1</sup> (APT), 806 cm<sup>-1</sup> (BPT) and 790 cm<sup>-1</sup> (HO-BPT) are lowered in frequency and sometimes weakened in intensity having splitted bands, upon complexation. This considerable shift on complexation is attributed to coordination of this keto sulphur. The disappearance of the stretching

TABLE I  
Electronic spectral data and relevant ligand field parameters

Complex	$\nu_1 \text{ cm}^{-1}$		$\nu_2 \text{ cm}^{-1}$		$\nu_3 \text{ cm}^{-1}$		$\beta$	LFSE Kcals/ mole
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.		
[Ni(APT) <sub>3</sub> Cl <sub>2</sub> ]	9875	10 D <sub>q</sub>	15800	fitted	27040	25674	0.76	33.86
		10 D <sub>q</sub>		16091		fitted	0.86	
		10 D <sub>q</sub>		16046		26794	0.85	
		10 D <sub>q</sub>		16153		27391	0.89	
[Ni(APT) <sub>2</sub> (CN) <sub>2</sub> ]	10106	10 D <sub>q</sub>	16720	fitted	26980	28816	0.96	34.83
		10 D <sub>q</sub>		16388		fitted	0.83	
		10 D <sub>q</sub>		16447		27253	0.85	
		10 D <sub>q</sub>		16289		26547	0.79	
[Ni(APT) <sub>2</sub> (OH) <sub>2</sub> ]	8890	10 D <sub>q</sub>	14000	fitted	25000	22318	0.62	30.48
		10 D <sub>q</sub>		14597		fitted	0.83	
		10 D <sub>q</sub>		14512		24488	0.79	
		10 D <sub>q</sub>		14698		25698	0.88	
[Ni(APT) <sub>2</sub> (NH) <sub>2</sub> ]	9800	10 D <sub>q</sub>	16000	fitted	26460	27008	0.87	33.60
		10 D <sub>q</sub>		15898		fitted	0.83	
		10 D <sub>q</sub>		15915		26545	0.84	
		10 D <sub>q</sub>		15873		26332	0.82	
[Ni(BPT) <sub>2</sub> ]Cl <sub>2</sub>	10300	10 D <sub>q</sub>	16780	fitted	27360	28184	0.90	36.31
		10 D <sub>q</sub>		16616		fitted	0.84	
		10 D <sub>q</sub>		16645		27495	0.85	
		10 D <sub>q</sub>		16568		27148	0.82	
[Ni(HO-BPT)Cl·H <sub>2</sub> O]	9500	10 D <sub>q</sub>	14850	fitted	26360	23516	0.63	32.57
		10 D <sub>q</sub>		15541		fitted	0.86	
		10 D <sub>q</sub>		15436		25774	0.81	
		10 D <sub>q</sub>		15667		27175	0.92	

and deformation of phenolic (OH) indicate the loss of phenolic proton on complexation, thereby implying metal-oxygen bond in (HO-BPT). The fact that coordination occurs through the terminal hydrazine atom and sulphur of the thio carbonyl group in thio-semicarbazide and thiosemicarbazones has been established by infrared measurements and X-ray structure determinations<sup>7</sup>.

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