

## Studies on the Complex compounds of Transition Metals with Isonicotinic acid Hydrazide

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### ABSTRACT

The complex compounds of isonicotinic acid hydrazide ( $C_6H_7ON_3$ ) with Ni (II), Cu (II), Fe (III) and CO (II) of type  $[ML_2(H_2O)_2SO_4]$  and with Pd (II) of type  $[ML_2Cl_2]$  have been prepared and characterized on the basis of elemental analysis as IR, UV and magnetic studies. The Ni (II), Fe (II) and CO (II)-complexes were found to be paramagnetic and octahedral, Cu (II)- complex was also paramagnetic but distorted octahedral, while Pd (II)-complex was found to be square planar and diamagnetic. Mycobacterial study of complexes showed Cu (II), Fe (II) and CO (III)-complexes to be poor inhibitory, while Ni (II) and Pd (II)-complexes inactive as whole.

### INTRODUCTION

Several acid hydrazides isolated as cited in literature of Jolly et al (1992) and depicted by several workers (Douthwaite, 1963; Grumbach 1966 and Schimdt et al 1962) as bacteriostatic and bactericidal, exclusively towards organism of the genus Mycobacteria. Their ligational property with metal ions and inhibitory activity of complexes are seldom depicted. Thus, in the present study, complexes of isonicotinic acid and hydrazide with Cu (II), Fe (II) and Pd (II) have been prepared, their structures were established and activity towards Mycobacteria was studied.

### METHODS AND MATERIALS

$NiSO_4.6H_2O$ ,  $CuSO_4.5H_2O$ ,  $FeSO_4.7H_2O$  and  $CoSO_4.7H_2O$  chemicals of EM and  $PdCl_2$  of AM grade were used as reagent for analysis. Isonicotinic acid hydrazide used in present work was a gift sample from Pfizer Ltd Nariman Point, Mumbai.

Elemental analyses were done by standard methods. Magnetic measurements were done by Guoy's balance. IR spectra of the ligand and complexes in KBr phase in the range 4000-200  $cm^{-1}$  were using Perkin Elmer Spectrophotometer No 621. Electronic spectra of complexes in methanol were recorded using Hilger Unispek Spectrophotometer No 20. There 0.01 M aq solutions of  $Ni^{+2}$ ,  $Cu^{+2}$ ,  $Fe^{+2}$  and  $Co^{+2}$  and 0.01 M solution of  $Pd^{+2}$  ions in 2 (M) HCl were used as standard solutions of metal ions. The 0.02 M solution of reagent in 60% aq ethanol was prepared. For complex preparation, equal volume of each of metal ion and reagent solutions were mixed slowly with stirring and digested on the water bath for about 1 hour. The crystalline complexes were cooled, filtered, washed 3-4 times with aqueous solution and dried over anhydrous  $CaCl_2$  in desicator to constant weight.

### RESULTS AND DISCUSSION

The pH value of complex formation, their colours, data on elemental analyses, magnetic moment values and absorption frequencies of electronic study have been placed in Table-1.

The complexes are soluble in methanol, carbon tetrachloride and ether. They are stable in air.

**Magnetic Moments:** The values of magnetic moments of Cu (II), Ni (II), CO (II) and Fe (II) suggested that they contain 1, 2, 3 and 4 unpaired electrons and they are paramagnetic. Zero magnetic moment of Pd (II) complex suggested it to be diamagnetic and square planar through dsp<sup>2</sup> hybridisation.

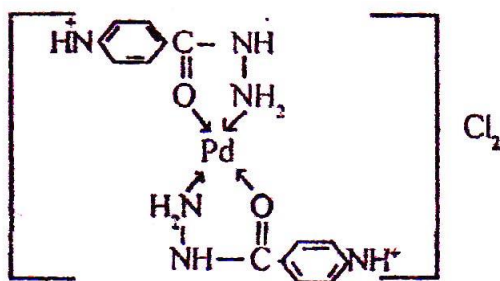
Complexes	pH value of Formation	Colors	Analytical data during study			Magnetic moment (BM)	V <sub>max</sub> cm <sup>-1</sup>
			% M present (Calcd)	% C present (Calcd)	% N present (Calcd)		
Ni (II)	3.5	Yellowish Blue	12.60 (12.63)	30.92 (30.98)	18.00 (18.07)	2.90	24875, 15300, 10965
Cu (II)	4.0	Green	13.29 (13.31)	30.60 (30.67)	17.82 (17.88)	1.80	13420, 25100
Fe (II)	4.0	Yellowish Brown	12.00 (12.09)	31.10 (31.17)	18.02 (18.08)	4.90	12190
CO (II)	3.5	Pink	12.60 (12.67)	30.90 (30.97)	18.01 (18.06)	3.87	21740, 19500, 8300
Pd (II)	3.0	Yellow	23.51 (23.57)	31.82 (31.90)	18.40 (18.60)	0.00	24390

**Electronic Spectra:** Electronic spectrum of Ni (II)-complex exhibits three bands at 24875, 15300 and 10965 cm<sup>-1</sup> which may be assigned to the transitions from 3A<sub>2g</sub> (F) to the three excited states; 3T<sub>1g</sub> (P), 3T<sub>1g</sub> (F) and 3T<sub>2g</sub> (F) respectively in OH symmetry. The band at 13420 cm<sup>-1</sup> in spectrum of the Cu (II) complex probably due to 2E<sub>g</sub>>2T<sub>2g</sub> transition and another at 25100 cm<sup>-1</sup> due to C>T transition suggest it to be distorted octahedral (7). The band at 12190 cm<sup>-1</sup> in spectrum of Fe (II) complex, analogue to 6T<sub>2g</sub>>5E<sub>g</sub> transition, suggests its octahedral geometry. The bands at 21740, 19500 and 8300 cm<sup>-1</sup> in CO (II)-complex may be assigned to the transitions from 4T<sub>1g</sub> (F) to 4A<sub>2g</sub> (F), 4T<sub>1g</sub> (P) and 4T<sub>2g</sub> respectively. The band positions suggested the octahedral structure of CO (II) complex (8). The band at 24390 cm<sup>-1</sup> in Pd (II)-complex is due to 1A<sub>1g</sub>>1B<sub>1g</sub> transition and is in accordance with the square planar.

**Infrared Spectra:** Only a few relevant bands on IR studies of the ligand and complexes were incorporated in Table 2.

L cm <sup>-1</sup>	Ni (II) cm <sup>-1</sup>	Cu (II) cm <sup>-1</sup>	Fe (II) cm <sup>-1</sup>	CO (II) cm <sup>-1</sup>	Pd (II) cm <sup>-1</sup>	Assignments
.....	3580 s	3350 s	3540 s	3560 s	.....	v(OH) of H <sub>2</sub> O
3560 m	.....	.....	.....	.....	.....	v (NH <sub>2</sub> )
3450 s	.....	.....	.....	.....	.....	v(NH <sub>2</sub> )
3380 ms	.....	.....	.....	.....	.....	H bonded NH stretch
.....	3370 bs	3380 bs	3380 bs	3375 bs	3370 bs	v(NH <sub>2</sub> )+ v (NH <sub>2</sub> )
3210 ms	3210 w	3210 w	3210 w	3210 w	3210 w	v(NH)
1650 s	1620 s	1630 s	1630 s	1635 s	1625 s	v(C=O)
995 w	995 w	995 w	990 w	995 w	995 w	v(N-N)
.....	785 s	790 s	780 s	785 s	.....	v (OH)
745 s	745 s	745 s	740 s	740 s	745 s	Mono substituted ring
.....	630 s	640 s	635 s	635 s	.....	Coordinated H <sub>2</sub> O
.....	530 w	520 ms	530 ms	540 ms	520 ms	v(M-O)
.....	520 w	510 bs	500 w	505 ms	505 ms	v(M-N)

The sharp bands at 3560 and 3450 cm<sup>-1</sup> in the spectrum of ligand may be assigned to v(NH)<sub>2</sub>, while medium sharp band at 3380 cm<sup>-1</sup> to H bonded (O...H-N) NH group. On complexation, NH<sub>2</sub> frequencies shifted downwards, superimposed NH frequency and appeared in complexes at broad sharp band at (3380-3370) cm<sup>-1</sup>. This showed that nitrogen atom of NH<sub>2</sub> group of hydrazide residue has coordinated to metal ions. The sharp bands at 3580-3540 cm<sup>-1</sup> and 640-630 cm<sup>-1</sup> in Ni (II), Cu (II), Fe (II) and CO (II)-complexes suggest the presence of coordinated water molecules. Some new bands at (540-520) and (520-500) cm<sup>-1</sup> in complexes only may be assigned to v (M-O) and v (M-N) as ascertained by (9-11) respectively. From these evidences, tentative structure of Pd (II) complex proposed is given below:



**Biological Study:** The ligand and complexes were tested in vitro for the anti-tubercular activity against virulent Mycobacteria using Agar diffusion microbiologic assay, based on Mycobacterium smegmatis. The ligand was found inhibitory in concentration as low as 0.02 mg/ml. The Cu (II), Fe (II) and CO (II)-complexes showed very weak inhibitory action, while the Ni (II) and Pd (II)-complexes showed complete inactivity for same concentration probably due to strong involvement of CO-NH-NH<sub>2</sub>-residue with metal ions in complexes.

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