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METAL COMPLEXES OF NICKEL, PALLADIUM AND PLATINUM WITH PYRAZOLYL PYRIDINE

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The complexes of 2-(Pyrazol-1'-yl) pyridine with Ni (II), Pd(II) and Pt (II) are reported. Stability constants were carried out by Job's method of continuous variation. The complexes were characterized on the basis of analytical data for metal determination by atomic absorption, elemental analysis, spectroscopic evidence and qualitative analysis by x-ray diffraction. The ligand forms a 1:1 complex with these metals.

Key words: Metal complexes, Nickel, Palladium, Platinum, Pyrazolyl, Pyridine.

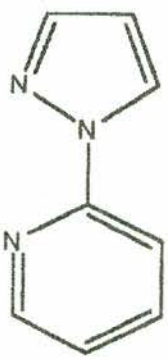
Introduction

Although several studies have been reported for metal complexes of Ni (II), Pd (II) and Pt (II) with a large number of organic ligands, Crow *et al* 1968; Reedijik 1970, 1971; Anagnostopoulos *et al* 1974; Phung *et al* 1976; Blais *et al* 1977; Bandini *et al* 1979; (Miguel *et al* 1994; Minghetti *et al* 1979; Trfimenko 1972) it was found that very little work had been carried out on metal-Pyrazol derivative complexes. Important groups of organic compounds form complexes with these metal ions, usually by co-ordination through one or more heteroatoms such as nitrogen. Such organic compounds may provide a class of compounds that are potential agents for identification and estimation of metals.

Literature survey shows that although complexes of various heterocyclic system have been reported (Xie *et al* 2000 Gianotio *et al* 2000; Zhang *et al* 2000) but virtually no work has been done on 2-(Pyrazol-1'-yl) pyridine metal complexes except a few recent publications (Mahmud *et al* 1999, 2000). The reagent 2-(Pyrazol-1'-yl) pyridine is somewhat at similar in structure as, 1,10-phenanthroline and 2,2'-bipyridyl. The work reported here is an effort to study these metal complexes with pyrazol derivatives.

Materials and Methods

All chemicals and solvents used were of Analar grade. Metal analysis was carried out on Varian atomic absorption spectrophotometer AA-1275. Infrared spectra were recorded on a Hitachi 270-30 spectrophotometer. All spectra were taken in KBr pellet. Stability constants were determined on UV/visible Hitachi U-2000 using glass cells of 1-cm thickness. Elemental analyses C,H,N was determined on a Coleman automatic analyser. X-ray diffractometer of Siemens D-5000 was used. All melting points were taken on Gallenkamp melting point apparents. 2-(pyrazol-1'-yl) pyridine (I) was prepared as reported (Khan *et al* 1970) as in the literature from pyrazole and 2-bromopyridine using cupric oxide as a catalyst.



(I)

General procedure (Jobs 1928). To the ligand solution in ethanol was added slowly metal chloride in ethanol. The reaction mixture was stirred under reflux. Crystals obtained were filtered off and washed several times with ethanol. The product was dried under vacuum over fused calcium chloride for 48 hours to get the Complex soluble in N-N-dimethyl formamide.

Procedure for the determination of stability constants. The solutions of ligands and metal solution were prepared according to the requirement of jobs method. In series of flasks

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the sum of the number of moles of ligands plus sum of the number of moles of metals were kept constant. The pH values were adjusted and their absorbance was measured at a λ_{max}, where neither the metal nor the ligand absorb but only the complex absorbs.

Results and Discussion

2-(Pyrazol-1'-yl) pyridine is a suitable compound for complex formation. The complexes formed were identified through their metal analysis, elemental analysis C,H,N, and infrared spectra (Table 1-3). The metal analysis of the complexes indicated the presence of metal in the ratio of 1:1 with ligand. The I.R. spectra of (I) (Khan *et al* 1981) and its complexes (II-IV) are given in Table 3. The C-H stretching frequency of the ligand (I) appeared at 2880 cm^{-1} while its 1630 cm^{-1}band was attributed to a C=N bonding (Nakamato 1963). The C-H bending vibraton was observed at 1350 $cm^{-1}$and C-C bonding vibration at 725 and 700 cm^{-1} and N-N band appeared at 1000 cm^{-1} (Brandt *et al* 1954).

These characteristic absorptions of the ligand (I) suffer some shifts to lower wave numbers on complex formation. The complex (II) shows lowering in C=N frequency to 1590 cm^{-1} with an appropriate appearance of a band below 625 cm^{-1} which may be attributed to the formation of Ni-N bond and is comparable to M-N stretching vibration for the complexes. (Schilt *et al* 1959). The Complex (III) also showed a lowering of C=N frequency to 1590 cm^{-1} which indicates the complex formation. The new bonds are due to (Pd-N) stretching vibrations and appeared at 640 cm^{-1} and 460cm^{-1}. (Harkin *et al* 1956). The complex (IV) showed an additional bond in the lower frequency region at 680 cm^{-1} and 520 cm^{-1} due to the formation of (Pt-N) bond in the complex. (Bertin *et al* 1958).

Job's method (Jobs 1928) was used to determine the stability constants of these complexes. At pH 4.5- 5.5, the formation of 1:1 (L:M) was found to take place with all the three metals. K_f values of these complexes were also calculated and are given in Table 4. Log K_f values are in the range of 7.57-8.00 which indicates that these complexes are fairly stable.

On the basis of analytical data (Table 2) and IR spectra (Table 3), the molecular formula for the complexes in general is

Table 1
Metal complexes of pyrazolyl pyridine

S No	Complex No	Colour	MP./DC	% Yield
1	II	Pink	142	67.7
2	III	Yellow	320	83.8
3	IV	Yellow	331	40.7

Table 2
Analytical data of complexes

S No	Comp No	Emperical formula	Mol wt	Calculated (%)				Found (%)				%M (cal.)	% M (found)
				C	H	N	Cl	C	H	N	Cl		
1	I	$C_8H_7N_3$	145	65.9	4.8	29.0	--	66.2	4.8	29.0	--	--	--
2	II	$(C_8H_7N_3)NiCl$	239.2	40.1	2.9	17.5	14.8	41.8	2.9	19.1	14.3	24.5	23.8
3	III	$(C_8H_7N_3)PdCl$	286.5	33.4	2.4	14.6	12.3	37.0	2.4	15.8	12.3	37.0	36.9
4	IV	$(C_8H_7N_3)PtCl$	375.5	18.3	1.8	11.1	9.4	18.0	1.6	11.7	9.5	51.9	51.2

Table 3
Infrared spectra of 2-(pyrazol-1'-yl) pyridine and its complexes

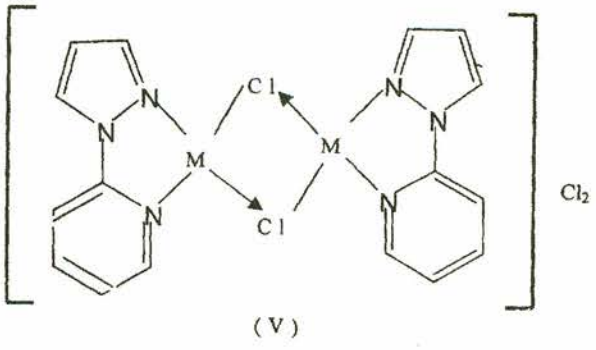
S.No.	Comp. No.	Aromatic ring		V (N -- N)	V (M -- N)
1	I	1600 s,	1530 m	950 ms	–
2	II	1590 ms,	1440 m	1080 m	620 w
3	III	1590 s,	1540 vs	1080 ms	460 ms
4	IV	1620 s,	1500 ms	1100 s	520 m

*In KBr pellet; vs = very strong; s = strong; m s= medium strong; m= medium, w=weak

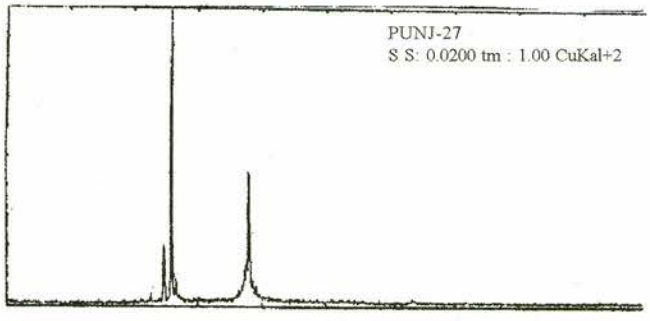
Table 4
Stability constants of complexes

Comp No	Ligand (10^{-4}M)	Metal ion (10^{-4}M)	K^*_f	L:M	Log K_f
II	1	Ni(II)chloride	10.100×10^7	1:1	8.0
III	1	Pd(II)chloride	5.550×10^7	1:1	7.57
IV	1	Pt(II)chloride	9.467×10^7	1:1	7.97

$$K^*_f = \frac{A/A_{ex}\ cm}{(\ cm\text{-}A/A_{ex}\ cm)\ (cL\text{-}A/A_{ex}\ cm)}$$

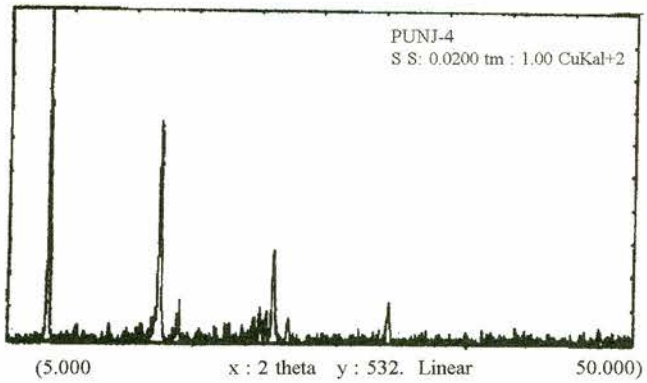


(V)



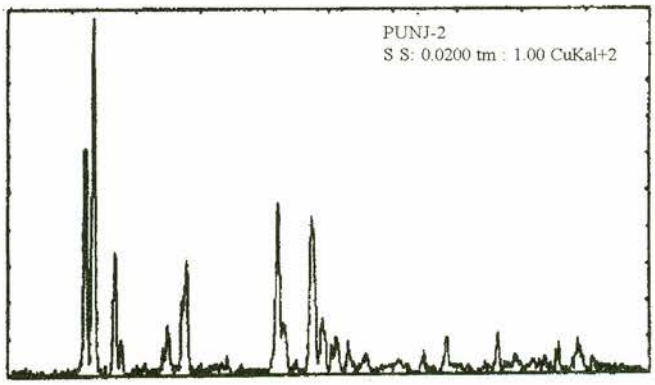
(5.000 x : 2 theta y : 2069. Linear 50.000)

Fig 1. XRD of 2-(pyrazol-1' -yl) pyridine.



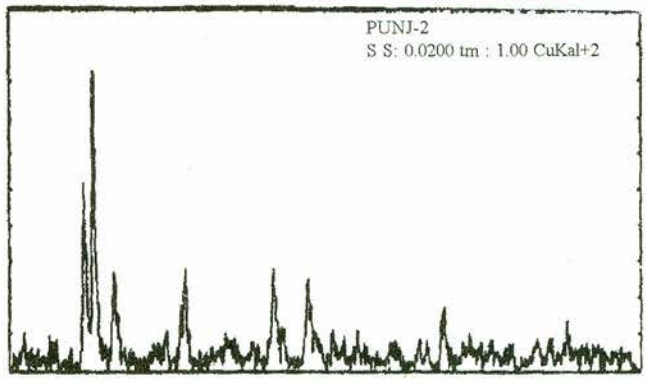
(5.000 x : 2 theta y : 532. Linear 50.000)

Fig 2. XRD of complex II.



(5.000 x : 2 theta y : 160. Linear 50.000)

Fig 3. XRD of complex III.



(5.000 x : 2 theta y : 79. Linear 50.000)

Fig 4. XRD of complex IV.

to be $(LMC1)_2$. The proposed structure is indicated as (V).

The X-ray diffractograph of the complex (II) formed from the reaction of 2-(Pyrazole-1'-yl) pyridine with Ni (II) Cl_2 is shown in Fig 1-2. The pattern does not show the peaks belonging to the starting materials. Similar pattern was indicated by complex (III) as shown in Fig 3. The complex (IV) as shown in Fig 4 indicates that new peaks of platinum complex have appeared which confirmed that these complexes have been formed.

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