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Cobalt(II), Nickel(II) And Copper(II) Complexes of 5–Methyl–3–[($2^{|}$)–$6^{|}$–Methyl Benzimidazolyl]Pyrazole

Manika Barar[*1]
[*1] *M.S.P.G College Saharanpur U.P ,India*

Abstract: *Synthesis, characterization Mass, IR, PMR and coordinating properties of a imidazolyl pyrazole viz 5-methyl-3-(2')-6'-methyl-benzimidazolyl) pyrazole (MBP) containing the well known chelating group –N=C-C=N- are reported.A host of electrolytic metallic complexes,* $M(MBP)_nX_2.2H_2O$ *(M= Co / Ni / Cu ,* **n** *= 2 or 3, X = a counter ion like* Cl^{-}, Br^{-}, NO_3^{-}, I^{-}, ClO_3^{-} *etc) of the ligand (* $C_{11}H_{12}N_4$ *) identified by physic- chemical techniques are described.*

Keyword: *5-methyl-3-[2'-6'-methyl benzimidazolyl] pyrazole, Mass, IR, PMR*

I. Introduction

Pyrazoles (1,2–diazole) is isomeric with imidazole (1,3–diazole) an integral part of the well known histidine molecule, which provides an important binding site in biological systems, playing a vital role in metal–protein interactions[1,2]**.** During a recent years a substantial amount of work has been generated around the studies involving the coordination characteristics of both imidazole and pyrazole derived (model) ligands from various aspects in order to have meaningful information regarding the binding sites of the in vivo metal ions.The vigorous development in the coordination chemistry of pyrazole based ligands has merited two review articles[3,4]. The report of the coordination pattern of ligands containing two different N–heterocycles by complexation with transition metal ion has enriched the literature**.**[5–8]

4–Acyl pyrazolones[9–13] have been shown to be good extraction reagents for metals in acidic solutions. Akama et al[14,15] in their systematic study of alkyl substituted 4–acyl derivatives of 3–methyl–1–phenyl pyrazol–5–one showed that due to its slightly lower pKa– value, the 4–benzoyl derivative (HPMBP) proved to be more efficient in the extraction of metal ions than the other 4–acyl pyrazolones studied. The pKa–values of the corresponding 4–trifluoroacetyl (HPMTFP) and 4–trichloro acetyl (HPMTCP) derivatives have been determined. These low values indicate that HPMTFP and HPMTCP many prove to be even more efficient reagents for metal extraction.Here we report the synthesis, characterization and coordinating properties of imidazolyl pyrazole viz 5–methyl–3–[$2^{|}$–($6^{|}$)–methyl benzimidazolyl] pyrazole (MBP) by complexation with transition metla ions.

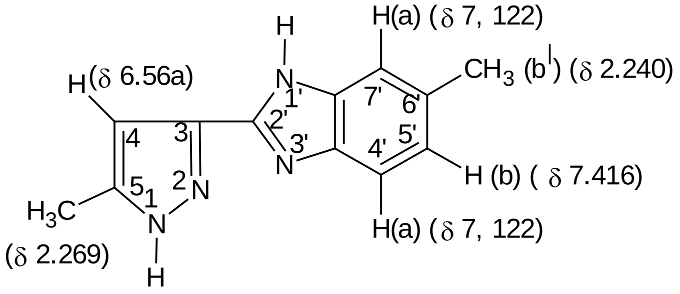


Fig. 1. 5–Methyl–3–($2^{|}$)–$6^{|}$–benzimidazolyl)pyrazole (MBP) ($C_{12}H_{12}N_4$)

II. Results And Discussion

The electron ionization mass spectrum of the title ligand, shows a molecular ion peak (M^+) at m/z 212 with 100% intensity (Fig. 2). This datum is happily compatible with the expected molecular weight of the compound, i.e. 212 which, in turn, agrees exactly with the molecular formula of the ligand. MBP, as ($C_{12}N_4H_{12}$) identical with its empirical composition as evidenced from C, H and N analyses. The other most prominent peak appears at m/z 212 with nearly 80% intensity; the less significant low intensity peaks are found at m/z 184 and 156. Based on the peak positions and their relative intensities, a fragmentation pattern can be formulated for the formation of different less stable components of the reported benzimidazolyl pyrazole. The envisaged fragmentation patterns or pathways are schematically shown in Fig. 3 with probable mechanisms which are self–explanatory. The mass spectral features along with the recommended fragmentation pathways support[16] the proposed structured formulation of the synthesized ligand as 5–methyl–3– ($2^{|}$)–$6^{|}$–methylbenzimidazolyl) pyrazole (Fig. 1).The pmr spectral data recorded in (DMSO–d_6) are in comfortable agreement with the proposed structural formulation of 5–methyl–3–($2^{|}$)–$6^{|}$–methylbenzi-midazolyl)pyrazole (Fig. 1, shown with δ values). A sharp three–proton singlet (Fig. 4) at δ 2.269 corresponds to three methyl protons at C–5 of pyrazole ring. The lone pyrazole proton at C–4 appears as a singlet at δ 6.568. The spectral signals at δ 2.464 and 3.344 are conceivably due to DMSO and HDO respectively. The aromatic protons (i.e. at $4^{|}$, $5^{|}$, $6^{|}$ and $7^{|}$ positions) of the benzimidazolyl moiety appear at δ 7.122, 7.416 and 7.547. A sharp two–proton singlet at δ 7.122, is due to $aa^{|}$ protons at C–$4^{|}$ and C–$7^{|}$, a doublet appearing at δ 7.416 and 7.547 are due to $bb^{|}$ aromatic protons of C–$5^{|}$ and C–$6^{|}$ positions of benzimidazole ring. The N–H protons of the pyrazole and the benzimidazole moieties do not appear in the pmr spectrum; this can be ascribed to its high lability and rapid deutero–exchange phenomenon in DMSO–d_6. Thus the pmr data unambiguously recommend the proposed structural formula of the title ligand, MBP . The reported bis– and tris–complexes of cobalt(II) conform to the general empirical composition, $Co(MBP)_2X_2$ (X = Cl^-, NO_3^-, ClO_4^-, I^-), $Co(MBP)_3X_2$ (X=Cl–, Br–, ½ SO_4^{2-}) as revealed from elemental analyses (Table 1). The molar conductance values (λ_m) of 115–203 Ω^{-1} cm^2 mol^{-1} for the methanolic solutions of all the Co^{II} complexes indicate their 1:2–electrolytic nature**[17]** at least in solution of the said solvent. The values for bis–species can be reconciled only in terms of complete solvolysis as

$$\mathbf{Co(MBP)_2X_2 + 2CH_3OH \rightleftharpoons Co(MBP)_2(OHCH_3)_2^{2+} + 2\,X^-}$$

where, X = Cl^-, I^-, NO_3^-, ClO_4^-. A lower $\wedge_m$ (115 Ω^{-1} cm^2 mol^{-1}) for the tris–cobalt(II) sulphate may be due to lesser ionic mobility of the anionic moiety. The μ_B values (Table 1) of the reported bis– and tris–cobalt(II) complexes lie in the range 4.29–4.91 B.M., the somewhat lower values (4.29–4.42 B.M.) for some of the species are ascribed to the presence of an orbital singlet ground state with a distorted octahedral environment**[18]**. The μ_B values can only suggest that the reported complexes belong to a group of lower symmetry (C_2). The diffuse reflectance spectra of the bis– and tris–cobalt(II) complexes are characterized by two main bands (except for $Co(MBP)_2I_2$) appearing at 8575–9165 and 20000–21275 cm^{-1} assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions(19) respectively, in a pseudo–octahedral environment. In case of $Co(MBP)_2I_2$, the ν_3 band (in terms of regular O_h symmetry) appears as a strong shoulder near 20000 cm^{-1}, which might be due tomixing with a CT band appearing near 27780 cm^{-1}. All the tris–complexes show this CT absorption near 27000–29000 cm^{-1} along with the bis–perchlorate where the band appears as a shoulder. The bis complexes show low intensity bands near 37000 cm^{-1}, which may be assigned as CT absorption associated with ligand $\pi \rightarrow \pi^*$ transitions. The values of LF parameters, Dq(973–1039 cm^{-1}), B (827–889 cm^{-1}) and β (0.85–0.91) for the reported complexes, calculated by known relationships**[20,21]** are consistent**[22]** with these observed for spin–free octahedral Co^{II} species reported earlier.

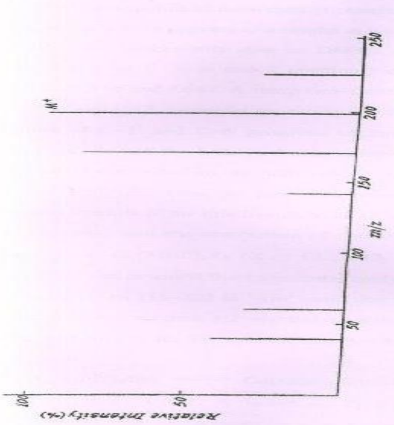


Fig 2 . : Mass Spectrum (70 eV) of 5-Methyl-3-(2'-6'- benzimidazolyl) pyrazole

The D.R.S. of $[Co(MBP)_2Cl_2]$ shows an intense shoulder near 16900 cm^{-1} which is not due to ν_2 transition, but is likely to arise from spin–forbidden transition**(73)** ${}^4T_{1g}(F)$–${}^4T_{2g}(G)$. The pink to orange solutions of the reported bis– and tris–complexes in DMSO exhibit spectral bands at 9090–10235 (ν_1) (ε = 40.1–87.9) and 20410–21710 cm^{-1} (ν_3) (ε = 25.0–47.7); the bis–iodo complex, however, shows no band in the ν_3 region possibly due to strong CT absorption in the same region.

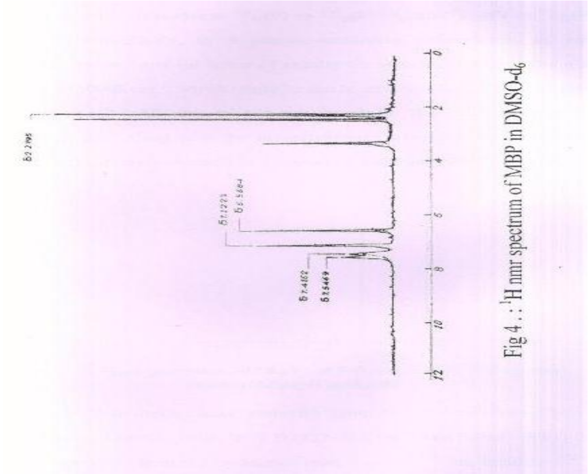
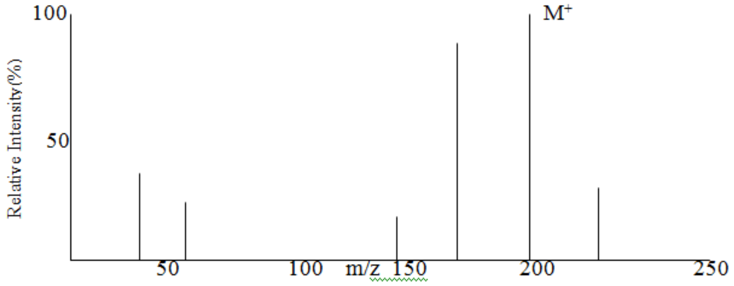
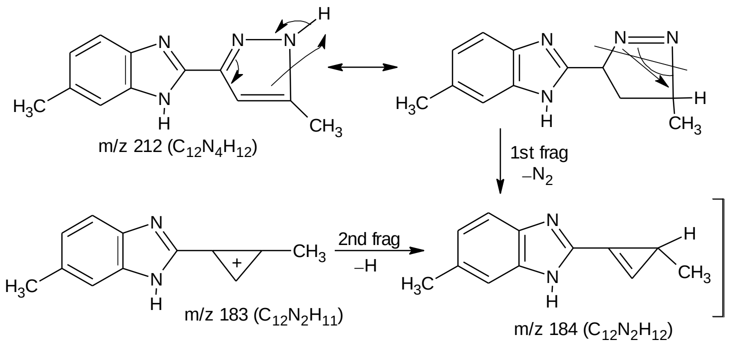


Fig 4 . : ^{1}H nmr spectrum of MBP in DMSO-d_6

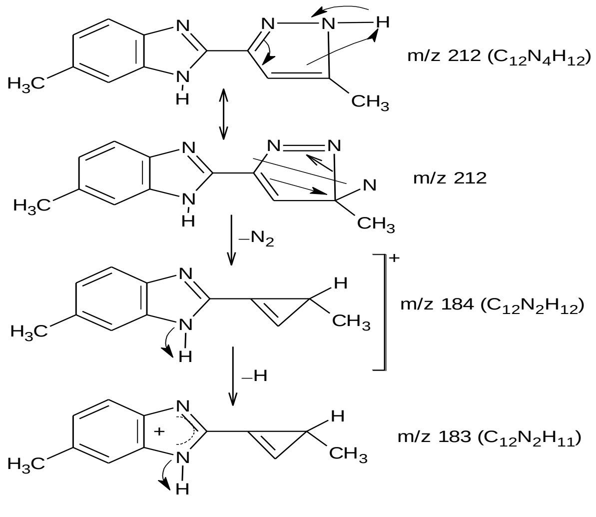


7.2) Mass Spectrum (0.70 eV) of 5–Methyl–3–(2|)–6|–methyl benzimidazolyl) pyrazole

Path I



Path II



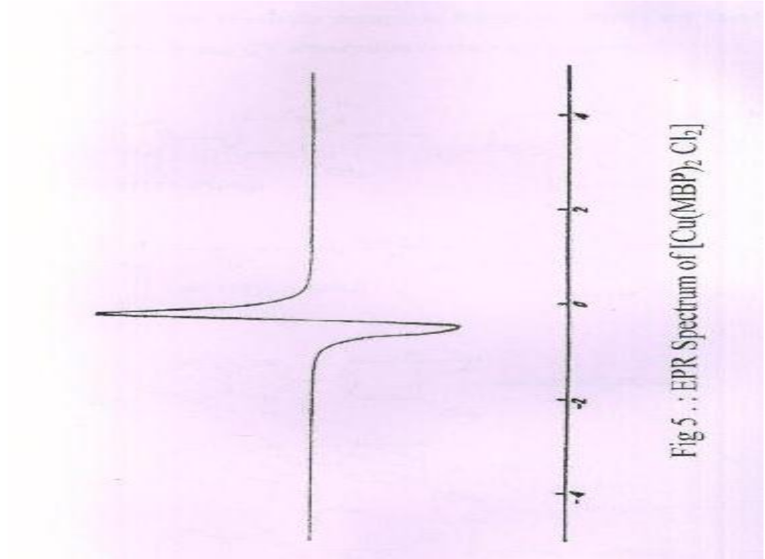


Fig 5 .: EPR Spectrum of $[Cu(MBP)_2 Cl_2]$

Path III

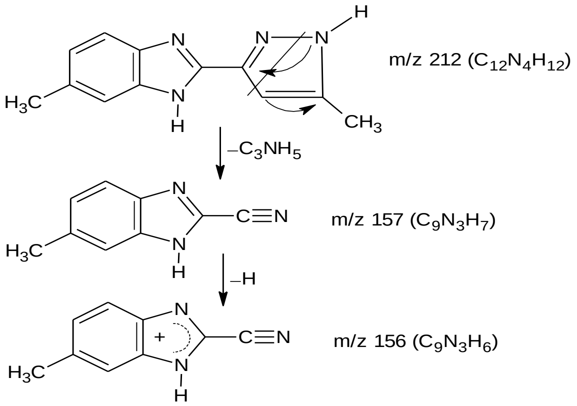


Fig. 3. Fragmentation pathways with probable mechanisms from the mass spectrum of MBP.

The The effective magnetic moment values (2.56–2.77 B.M.) at 30° for $[Ni(MBP)_3]X_2$ and $[Ni(MBP)_2X_2]$ are grossly commensurate with six–coordinate spin–free Ni^{II} complexes**[24].** The molar conductance values in methanolic solutions lie in the range 154–159 (bis–complexes) and 194–218 Ω^{-1} cm^2 mol^{-1} (tris–species classifying the reported species as 1:2 electrolytes**(12)** in the said solvent. The diffuse reflectance spectra of all the reported. Ni^{II} species consist of three main bands appearing at 10205–10415, 17095–18180 and 26660–28570 cm–1 assignable**[25]** to transitions ν_1, ν_2 and ν_3 respectively, in a regular O_h symmetry. The ν_3 band due to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition appearing in the range 26660–28570 cm^{-1} trail to the higher energy UV–region, this is possibly due to its mixing up with CT absorption. The calculated**[26]** band (ν_3) positions are very near to the observed ones, and hence, the assignment might be taken as reasonably correct. The weak spectral bands appearing as shoulders around 13700–13890 cm^{-1} for tris–chelates of Ni^{II} may be attributed to spin–forbidden transitions**[27]**. For the bis–chelates, a high intensity band appears in the uv region (31250 cm^{-1}) which may be assigned as CT absorption associated with ligand $\pi \rightarrow \pi^*$ transition. The LF parameters calculated from the diagonal sum rule**[28]** (assuming O_h symmetry) furnish values of Dq (1020–1042 cm), B (900–991 cm^{-1}) and β (0.83–0.92) adding tacit support for the proposed octahedral geometry**(28)** for the reported Ni^{II} species.

The values of ν_1/ν_2 lying in the range 1.66–1.78 offer further evidence for an octahedral environment.(29) Electronic spectral data of the methanolic solutions of the Ni^{II} complexes consist of two main bands located at 10205–10870 and 16130–18180 cm^{-1} which may conceivably be assigned to ν_1 and ν_2 transitions in an average O_h symmetry. The calculated molar extinction coefficients of the order of 11.2–22.7 cm^{-1} mol^{-1} give additional support to the octahedral arrangements**[29]** of the ligands in the metal chelates. The absence of the ν_3 band in the spectral data in solution may be due to an intense internal $\pi \rightarrow \pi^*$ transitions of the ligand or due to CT absorption, arising from M→L via the π–antibonding level of the heterocyclic ligand(s)**[30]**.

The strong band at 33785 cm^{-1} with high molar extinction values (ε = 157.6–194.0 cm^{-1} mol^{-1}) in the spectra of the bis–chelates of Ni^{II} in methanol may originate from charge transfer.

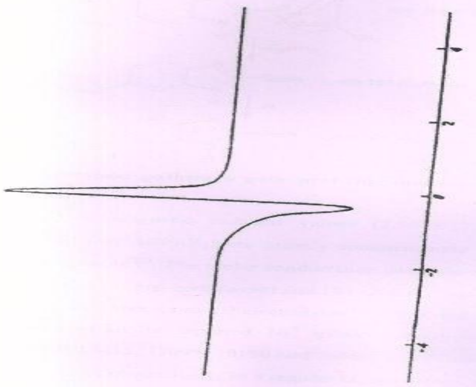


Fig 6 : ESR Spectrum of $[Cu(MBP)_2(OH_2)_2](ClO_4)_2$

The bis complexes, $Cu(MBP)_2X_2.nH_2O$ (X = Cl^-, Br^-, ClO_4^-, NO_3^-, BF_4^- and and 1/2 SO_4^{2-}, n = 0.2) show λ_m values in the range 71–193 Ω^{-1} cm^2 mol^{-1} in DMF (Table 1) classifying the complexes either as 1:1 or 1:2 electrolytes(16) depending upon the extent of solvolysis due to either partial or total release of anions(X) in the said solvent. The μ_B values of 1.72–2.12 B.M. at 30° for the reported Cu^{II} complexes are in accord with their distorted octahedral configuration(31) as expected. The diffuse reflectance spectra of $Cu(MBP)_2X_2.nH_2O$ are characterized by a broad asymmetric band appearing around 14925–15875 cm^{-1} suggesting that all the three expected transitions, $^2B_{1g} \rightarrow {}^2A_{1g}(\nu_1)$. $^2B_{1g} \rightarrow {}^2A_{2g}(\nu_2)$ and $^2B_{1g} \rightarrow {}^2E_g(\nu_3)$ in D_{4h} symmetry lie within one broad envelope and that distortion is not appreciable from octahedral symmetry. A recognizable band around 27025–27395 cm^{-1}, probably originating from charge transfer has been observed in the d.r.s. of all the reported Cu^{II} complexes. All the bis–Cu^{II} complexes of MBP are reasonably regarded as tetragonally distorted octahedral**[32,33]**. The DMSO solutions of the Cu^{II} 15105 cm^{-1} indicating that there is no significant change in the stereochemistry of the complexes on dissolutioin even in a donor solvent.

Table 2: EPR Spectral Data of some Cu^{II} complexes

S.No.	**Compd.**	$g_{|}$	$g_{||}$	g_{av}	**G**
1.	$[Cu(MBP)_2Cl_2]$	2.062	2.151	2.091	2.43
2.	$[Cu(MBP)_2Br_2]$	2.042	2.191	2.092	4.54
3.	$[Cu(MBP)_2(NO_3)_2]$	2.032	2.121	2.062	3.78
4.	$[Cu(MBP)_2(OH_2)_2](ClO_4)_2$	2.032	2.218	2.064	4.00

MBP ($C_{12}H_{12}N_4$)

The EPR data (Table 2) on some of the reported Cu^{II} complexes have been interpreted according to Kneubuhl's method**[34]**. The data along with representative spectral curves (Fig. 5 and 6) are useful for estimating the presence or absence of significant exchange coupling**[35]**.

As the G values for the bromo– and the perchlorate–complexes are ≥ 4, their exchange coupling is less than those in other two cases. The exchange coupling might be considered as feeble in $[Cu(MBP)_2(NO_3)_2]$ having a G value of 3.78, but for the chloro–complex, high exchange coupling is present (G = 2.43). It is clear, therefore, that the degree of exchange coupling is dependent on the counterion (X) in the examined Cu^{II} species. The data also clearly reveal that in all the cases $g_{||} > g_{|}$ which is characteristic of tetragonal symmetry with $dx^2–y^2$ ground state.**(35)** Again the value of 2.092 ≥ gav 2.062 points out unambiguously for a tetragonally distorted octahedral symmetry with a $dx^2–y^2$ state rather than dx^2. The structural formulation of the ligand MBP (Fig. 1) and construction of molecular model of the same suggest that the tertiary nitrogen atoms of the pyrazolyl– and the imidazolyl–ring systems are the only available bonding sites for complexation with a metal ion forming a stable five–membered ring. This expectation is indirectly shown to be true from significant changes in the ir band frequencies in the metal complexes compared to those of the free ligand.

Table 1: Analytical and Spectral Data of Complexes

S. No.	Compd.	Colour	Yield %	Analysis %; Found (Calcd.)					$\mu^{*}_{eff.}$ B.M.	Λ_M^{**} Ω^{-1} cm^2 mol^{-1}
				Metal	C	H	N	X		
1.	$[Co(MBP)_2Cl_2]$	Pink	75	10.52(10.64)	51.84(51.99)	4.20(4.33)	20.03(20.21)	12.70(12.81)	4.29	150
2.	$[Co(MBP)_2(NO_3)_2]$	Pink	65	9.60(9.71)	47.30(47.45)	3.80(3.95)	22.92(23.06)^a	–	4.35	203
3.	$[Co(MBP)_2(ClO_4)_2]$	Pink violet	55	8.50(8.64)	42.10(42.23)	3.40(3.51)	16.27(16.42)	10.29(10.41)	4.34	167
4.	$[Co(MBP)_2I_2]$	Yellow	60	7.82(7.99)	38.35(39.08)	3.15(3.25)	15.0(15.19)	34.32(34.41)	4.80	198
5.	$[Co(MBP)_3Br_2]$	Pale pink	55	6.93(6.89)	50.60(50.52)	4.27(4.21)	19.75(19.65)	19.01(18.71)	4.40	174
6.	$[Co(MBP)_3]SO_4$	Light pink	60	7.32(7.45)	54.48(54.61)	4.40(4.55)	21.10(21.24)	3.91(4.04)^b	4.42	115
7.	$[Co(MBP)_3]Cl_2$	Pink	55	7.50(7.69)	56.22(56.49)	4.60(4.70)	21.80(21.93)	9.10(9.26)	4.41	187
8.	$[Ni(MBP)_3](Cl_2)$	Bluish violet	65	7.50(7.66)	56.30(56.41)	4.60(4.70)	21.80(21.94)	9.10(9.27)	2.61	134
9.	$[Ni(MBP)_3](NO_3)_2$	Bluish violet	65	7.0(7.17)	52.63(52.76)	4.25(4.39)	23.82(23.94)^a	–	2.77	194
10.	$[Ni(MBP)_3]I_2$	Grey yellowish	65	6.0(6.18)	45.38(45.53)	3.63(3.79)	17.60(17.70)	26.60(26.77)	2.67	189
11.	$[Ni(MBP)_3](ClO_4)_2$	Bluish violet	65	6.40(6.56)	48.20(48.20)	3.84(4.02)	18.65(18.79)	7.80(7.94)^b	2.72	218
12.	$[Ni(MBP)_3](BF_4)_2$	Blue	75	6.63(6.76)	49.60(49.75)	4.0(4.14)	19.16(19.34)	–	2.60	208
13.	$[Ni(MBP)_2](SCN)_2$	Blue	60	10.2(9.80)	52.0(52.11)	3.85(4.0)	23.20(23.38)	10.53(10.68)	2.56	154
14.	$[Ni(MBP)_2Br_2]$	Light Blue	60	9.0(9.13)	44.70(44.81)	3.60(3.73)	17.30(17.42)	24.70(24.89)	2.67	159
15.	$[Cu(MBP)_2Cl_2]$	Light green	50	11.20(11.37)	51.39(51.56)	4.15(4.29)	19.39(20.03)	11.57(12.71)	1.72	193
16.	$[Cu(MBP)_2Br_2]$	Dark green	60	9.67(9.81)	44.31(44.47)	3.60(3.70)	17.12(17.29)	24.60(24.70)	1.92	70
17.	$[Cu(MBP)_2(NO_3)_2]$	Deep green	60	10.22(10.39)	46.85(47.09)	3.80(3.92)	22.72(22.89)^a	–	1.88	133
18.	$[Cu(MBP)_2(H_2O)_2]\ (ClO4)_2$	Yellowish green	75	8.60(8.79)	39.70(39.64)	3.72(3.87)	15.40(15.50)	9.70(9.82)^b	1.84	137
19.	$[Cu(MBP)_2(BF_4)_2]$	Bright green	50	9.48(9.61)	43.42(43.56)	3.50(3.63)	16.80(16.94)	–	1.80	80
20.	$[Cu(MBP)_2SO_4]\ 2H_2O$	Green	60	10.10(10.25)	48.40(46.48)	4.37(4.51)	17.90(18.07)	5.01(5.16)^b	2.12	113

*At 303 K, ** In 1.0×10^{-3} M methanolic solution for Co^{II} and Ni^{II} or DMF solution for Cu^{II} complexes
^{a}Including N present in nitrate; ^{b}S%; ^{c}including N present in thiocyanate.
MBP = $(C_{12}H_{12}N_4)$

A strong band appearing at 1570 cm^{-1} (in the uncomplexed ligand spectrum) assigned to $\nu_{C=N}$ of the diazole systems is shifted towards higher frequency region ($\Delta\nu$ = 5–15 cm^{-1}) in its metal complexes, indicating thereby the expected participation of both pyrazolyl and imidazolyl ring nitrogens**[36]**. Similar positive shifts of $\nu_{C=N}$ vibrations have previously been reporte**d[37]** for transition metal complexes of N–heterocyclic bases; ν_{N-N} of the pyrazole ring also suffers positive shift ($\Delta\nu$ = 5–30 cm^{-1}) indicating tacit support to the participation of the tertiary pyrazolyl nitrogen. In the far–ir spectra, the appearance of bands appearing around 300 cm^{-1} (290–320 cm^{-1}) can safety be assigned to $\nu_{M=N}$(diazole(38). The ir spectral data also furnish meaningful clues with regard to the mode of attachment of counterion (X) in the reported metallic complexes. Some of the characteristic and relevant anion frequencies with probable assignments and approximate symmetry**[39]** are sorted out in Table 3. It is revealed that in the all the tris–species, the counterion (X) obviously retains its ionic character while in the bis–complexes of MBP, the anionic component (Cl^-, Br^-, NCS^-, BF_4^-, ClO_4^- and SO_4^{2-} is coordinated except in $[Cu(MBP)_2–(OH_2)_2](ClO_4)_2$ where it (X) retains ionic character. It is reasonably inferred, therefore, that for the tris–chelates of the primary ligand (MBP), is exhibited a neutral bidentate function all the six positions of the octahedron being occupied by the donor nitrogens**[40–42]** of the three molecules of the title ligand (MBP), while for the bis–species, two primary ligand molecules (MBP) occupy four positions of the octahedron and the trans– axial sites are taken up either by the coordinated anions or water molecules, although such propositions are highly conjectural in absence of X–ray crystallographic data**.[43–45]**

III. Experimental

Materials: All the chemical used were B.D.H. quality. Metal(II) bromide, iodide, perchlorate, fluoborate and thiocyanate were either generated in situ or prepared from metal(II) carbonates and the appropriate acids/salts and were used after recrystallisation. Spectrograde solvents were used for spectral and conductance measurements.

5–Methyl–3–[(2|)–6|–methylbenzimidazolyl)pyrazole:Thetitleligand, –methyl–3–(2|)–6–methylbenzimidazolyl) pyrazole (MBP) was prepared by solid state condensation around 130–60° of 4–methyl phenylenediamine (0.1 mol) and 5(3)–methylpyrazole–3(5)–carboxylic acid**(46)** (0.1 mol) following the general method of synthesis of benzimidazole derivatives with proper modifications. The shinning white needle–shaped crystals of the pure product was recrystallised from ethanol, m.p. 309–10° (Found: C, 67.80; H, 5.50; N, 26.30; $(C_{12}N_4H_{12})$ calcd. For: C, 67.92; H, 5.66, N,26.41%).

Preparation of the Co^{II}, Ni^{II} and Cu^{II} salts with MBP: Both tris–and bis–complexes of Co^{II}, Ni^{II} and and Cu^{II} with different counterions were prepared by interaction of the ligand, MBP and the hydrated metal(II) salt, $MX_2.nH_2O$, in appropriate mole ratio (0.003 : 0.001 for tris–species and 0.002 : 0.001 for bis–species) in hot ethanolic solution (except in the case of sulphate complexes, where water was used as solvent). In case of both bis– and tris–complexes of Co^{II} and Ni^{II}, refluxing was necessary for −1 h and the concentrated refluxate on cooling to room temperature (25°) precipitated the desired complex as microcrystalline coloured product (Table 1), while $Cu(MBP)_2X_2$, in each case, was obtained within few minutes of mixing the ligand and the Cu^{II} salt in aqueous ethanolic solution. All the solid complexes were collected and dried as usual. C, H, and N were estimated in a Perkin–Elmer 240 elemental analyzer or in a Thomas CH Analyser 35. The metal contents were determined by conventional gravimetic methods, viz. nickel as nickel(II) dimethyl glyoximate, cobalt as anhydrous cobalt(II) sulphate and copper as $Cu(en)_2HgI_4$. The anions (halogen, sulpahte etc.) were estimated by standard procedure.(47)

Table 3: Some Characteristic Anion Frequencies with Probable Assignments) and Approximate symmetry for the complexes

S. No.	**Complex**	**Anion bands (cm^{-1})**	**Assigments**	**Symmetry**
1.	$[Co(MBP)_3]SO_4$	1150–1060bs	ν_3 of an ionic sulphate	T_d
2.	$[Ni(MBP)_3](ClO_4)_2$	1100–1095bs 630bs	ν_3 of an ionic perchlorate ν_4	T_d
3.	$[Ni(MBP)_3](NO_3)_2$	1405–1380bm 815bs	ν_3 of an ionic nitrateν_4	D_{3h}
4.	$[Co(MBP)_2Cl_2]$	280m	$\nu_{Co–Cl}$	–
5.	$[Ni(MBP)_2Br_2]$	285s	$\nu_{Ni–Br}$	–
6.	$[Cu(MBP)_2Cl_2]$	280s	$\nu_{Cu–Cl}$	–
7.	$[Co(MBP)_2(ClO_4)_2]$	1185m 1115w 1090s 1035m 625bs	ν_1 Splitted ν_3 of σ–bonded perchlorate ν_4	C_{3v}
8.	$[Cu(MBP)_2(H_2O)_2]$ $(ClO_4)_2$	1130–1070bs 630vs	ν_3 of anionic perchlorate	T_d
9.	$[Co(MBP)_2(NO_3)_2]$	1400bm 1310m 820m	Components of ν_3 of monodentate nitrate ν_2	C_{2v}
10.	$[Cu(MBP)_2SO_4].2H_2O$	1160vs 1100vs 1050vs 1010s	Splitted ν3 of bonded sulphate ν_1	C_{2v}
11.	$[Ni(MBP)_2(SCN)_2]$	2100bs 810s 470cm^{-1}	ν_1(νC=N stretching) ν_3(νC–S stretching) of N–bonded thiocyanate νNCS)	–
12.	$[Cu(MBP)_2(BF_4)_2]$	1095m 1050s 1035m	Splitted components of ν_3 of a monodentate fluoborate	C_{3v}

MBP ($C_{12}H_{12}N_4$)

Mass spectrum was recorded on an AEIMS spectrometer (70 eV), pmr spectrum (DMSO–d_6) on a Brooker AM 300 L superconducting FT NMR spectrometer (300 MHz) and esr spectra (solid state) on a Varian EPR E 112 spectrometer. Various physicochemical measurements such as magnetic susceptibility, molar conductance, electronic (both D.R.S. and solution) and IR spectra studies were carried out by the reported methods.

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