

INTRODUCTION TO THE PRESENT WORK.

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The characteristics of pyrazoles and their metallic complexes have been discussed and the important work in this field has been reviewed in the foregoing section.

In the present investigation, 3,4,5-trimethylpyrazole (Tmpz) has been chosen as the ligand with a view to study its complex-forming ability with transition metal ions. No work has yet been reported with this particular ligand. The trialkyl pyrazole i.e. 3,4,5-trimethylpyrazole has been found to act as a monodentate ligand like disubstituted (3,5-dimethyl) pyrazole.

From the discussions in the foregoing section, it is now well-established that the pyrazole molecule coordinates to the metal ions through its tertiary nitrogen atom. So it is reasonable to accept, in analogy, that 3,4,5-trimethylpyrazole (Tmpz) will also coordinate through its tertiary nitrogen atom in forming the metal complexes.

The ligand (Tmpz) forms well-defined crystalline complexes with Cu (II), Ni (II) and Co (II) ions. Three types of metallic complexes of Tmpz have been isolated and studied in detail. These are of the types MX_2 , ML_2X_2 , and ML_4X_2 ; where X = anions like Cl^- , Br^- , I^- , BF_4^- , ClO_4^- , NO_3^- , SCN^- , and $\frac{1}{2}SO_4$.

L = a molecule of Tmpz.

M = Cu (II), Ni (II) and Co (II) ions.

MLX_2 type of complexes were obtained in the case of Cu (II) ~~only~~ ion. only. Attempts to prepare complexes of the type ML_6X_2 ended in failure and this is attributed to steric reasons. Complexes of the type ML_3X_2 could not also be isolated although the indication of their formation was obtained from thermal studies. The complexes have been characterised by their chemical analyses, magnetic moment values, conductance data as well as their electronic and infrared spectra. Thermal stabilities of the complexes have also been studied qualitatively. The magnetic moment values of the complexes in the solid state and the molar conductance values of the complexes in different solvents were measured at room-temperature ($\sim 30^\circ C$). The electronic spectra in different solvents, both coordinating and non-coordinating, have been recorded to ascertain the different stereochemistries of the complexes.

The i.r. spectra of the ligand has been reported¹ in KBr pellets. As in the present investigations the infrared spectra of the metallic complexes were recorded in nujol-mull, the i.r. spectra of the ligand was also recorded in nujol-mull, using NaCl-prism employing the usual technique². In this spectrum of the ligand the N-H vibration is found at $3175-3120\text{ cm}^{-1}$. The aromatic C-H stretching vibrations and those of the CH_3 -group are found at 3096 cm^{-1} . At $2970-2855\text{ cm}^{-1}$, the broad and diffused absorption bands typical for hydrogen-bonded structure^{are} obtained. A characteristic band used in the spectral diagnosis of a trialkyl substituted pyrazole is obtained at 1592 cm^{-1} with a weak shoulder at 1578 cm^{-1} ; and that at $1525-1508\text{ cm}^{-1}$ together with a doublet can be regarded as typical for the tri-substituted structure. A strong, sharp band at 1375 cm^{-1}

indicates the rocking of the CH_3 -group or one of the bending modes of the pyrazole skeleton. Several bands of medium intensity are obtained in the range $1250\text{-}900\text{ cm}^{-1}$. 1155 cm^{-1} band is typical for trimethylpyrazole, and the band at 1115 cm^{-1} is suggested as being useful for the diagnosis of a polysubstituted pyrazole. Another band at $1002\text{-}945\text{ cm}^{-1}$ is obtained and this is probably due to the ring vibration of the pyrazole ring. The band at about 755 cm^{-1} is strongly prominent as a doublet, which has been assigned as one of the out of plane deformations of the ring. Another band of medium-intensity is obtained at about 640 cm^{-1} which could not be assigned with any certainty. Direct metal-ligand stretching frequencies could not be recorded since they are beyond the range of the spectrophotometer used.

Bibliography:

1. G. Zerbi and Carlo Alberti : Spectrochim. Acta : 1963, 19, 1261-73.
2. J. R. Wason : Chem. Analyst : 1967, 56, 36.