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Research Article

SYNTHESIS AND STRUCTURAL INVESTIGATIONS OF COORDINATION COMPOUNDS OF PALLADIUM WITH 2-METHYL IMIDAZOLE

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ABSTRACT

The paper emphasized on a new series of mixed ligand co-ordination compound of Palladium having square planner stereochemistry, around the metal ion with the general formula ,$[PdL_2Cl_2]$ where L= 2-methyl Imidazole has been isolated in the solid state by the interaction of with the aforesaid ligands. The synthesized co-ordination compound has been characterized by elemental analysis, electrical conductance, magnetic measurements, molecular weight determination, electron spin resonance, infra red spectral measurements and NMR studies. A square planner structure has been proposed for the complex. It is observed that:

The synthesized compound is brown in colour, non hygroscopic, soluble in DMF, DMSO, slightly soluble in acetonitrile and sparingly soluble in other solvents. The complexes thermally stable and do not decomposed up to 260^0C. The complex has d^8 configuration and show anti tumor activity.

Keywords: Complex, Palladium, 1-methyl imidazole, Anti tumor activity

INTRODUCTION

2-Methyl imidazole represents one of the most active classes of compounds possessing wide spectrum of antitumor activities. It prepared from glyoxal and ammonia and, to indicate its source, proposed the name glyoxalin. This name is still used in the modern literature especially by British workers. The name imidazole, used in present monograph is due to Hantzsch. He classified as azoles the five membered Polyheteroatomic ring system containing at least one tertiary nitrogen. The term imidazole implies a five membered, heterocyclic ring system containing in addition to tertiary nitrogen, an imino group; just as the names oxazole and thiazole designate five membered ring systems containing in addition to tertiary nitrogen an oxygen or sulphur atom. Fig-1

The imino nitrogen receives position 2, and the numbering follows around the ring so as to assign the smallest possible number to the tertiary nitrogen , which is designated s position 3.The substituted nitrogen represents the starting point for the numbering of the N-substituted imidazoles. The designation of a substituent in position 2 offers no problem because of the symmetrical location with respect to the nitrogens. The naming becomes somewhat more complex, however, when substituent ids introduced in to the 4 or 5 position. Depending upon the position of the imino hydrogen such a compound must be designated as either a 4 or a 5 –monosubstituted imidazole, the tautomeric character of the imidazole precluding a definite assignment of structure. Such compounds are designated as 4 (or 5) monosubstituted imidazole.The presence in the imidazole structure of acidic pyrrole nitrogen and basic pyridine nitrogen explains the amphoteric nature of these compounds. Qualitatively, the imidazole may be regarded as a "cross" between a pyridine and a pyrrole. Thus one could expect a deactivating influence toward electrophilic reagents caused by the pyridine nitrogen, which to a certain degree is offset by the electron releasing properties of the pyrrole nitrogen. The chemical behaviour of the imidazole is in agreement with this admittedly crude picture.

MATERIALS AND METHODS

2-methyl Imidazole was procured from Aldrich Chemical Company, U.S.A. and used as such.$PdCl_2$ was obtained from TOKYO KASEI Organic Chemical, Japan and B.D.H England. Distilled water used in all the operations.

Preparation of the complex

Preparation of [Pd (2 – Methyl Imidazole)$_2$ Cl$_2$]

Palladium (II) complex with 2- Methyl Imidazole were prepared by mixing 0.1 N HCl solution of $PdCl_2$ with methanolic solution of the Imidazole (0.112mol) and heating the reaction mixture was refluxed on a water bath for 2 hours .The complex precipitated out in neutral medium on cooling .It was filtered ,washed several times with hot methanol and dried in vacuo over fused calcium chloride.

$$[Pd(Cl)_2] + 2L \xrightarrow[H_2O]{CH_3OH} [Pd(L_2)(Cl)_2]$$

Where L = 2-Methyl Imidazole

Analysis of constituent's elements

(i) Carbon, hydrogen, nitrogen and oxygen present in the investigated complexes were estimated micro analytically.

Estimation of palladium

For the estimation of Palladium as Palladium 1, 2, 3 benzotriazole, the synthesized compound solution were mixed with 10ml of 2M. Acetic acid- sodium acetate buffer and 5ml of 4% EDTA solution.. Then 2.5 % acetic acid, was added with shaking. Digest the solution between 60^0C-90^0C, are 20 minutes. The resulting precipitate was filtered (G 3), washed several times with very dilute HCl (1:100), finally with distilled water and dried to a constant weight at 110^0C.

RESULTS AND DISCUSSION

Magnetic measurements

The magnetic values of the synthesized complex measured at room temperature. The magnetic moment value of the complex is zero. Hence, It is diamagnetic. The square planar geometry of the complex is evident from their diamagnetic nature.

Conductance measurement

The value of molar conductance are in the range 0.052-0.058 Ω^{-1} cm^{-1} mol^{-1} suggesting non electrolyte nature of the synthesized complex. Solubility of the complex in various temperatures in benzene is given in table number **1.**

Infrared spectroscopy

The important infrared spectral bands of the synthesized complex containing coordinated 2-methyl Imidazole presented in **table 2**.

The ligand 2-methyl Imidazole possess two possible donor sites, two cyclic nitrogen ring system. Further that the cyclic nitrogen atom involved in coordination through the N atom. The IR frequency of tertiary cyclic nitrogen ring is essentially changed, thereby, suggesting that the cyclic nitrogen of this ligand participate in the coordination. Coordination through the ring nitrogen present in the

Imidazole ring causes an increase in the ring ν (CN) and Imidazole ring breathing mode. In the uncoordinated ligand, the Imidazole ring breathing mode appears at 1329 cm^{-1} . The significant positive shift for Imidazole ring breathing mode in the synthesized complex with 2-methyl Imidazole indicates conclusively that coordination of the ligand takes place through Imidazole ring nitrogen only.

Electron spin resonance spectra

The electronic spectral bands of the complex **(table 2)** were assigned.The molecular orbital approach was used to explain the structure of square –planar complex of the d^8 element. The metal orbital's involved in σ bonding in square planer complex is the ndz^2, $ndx^2\text{-}y^2$, $(n+1)P_x$ and $(n+1)P_y$. Nevertheless, judging from the values of the overlap integrals, $nd_{x2\text{-}y2}$ (n+1)s, $(n+1)P_x$ and $(n+1)P_y$ account for most of the σ – bonds , and ndz^2 makes only a minor contribution. The most important π- molecular and a combination of π orbital is of the ligand. The correlation of the bands observed in the electronic spectra for the studied complex with those of $[M(CN)_4]^{2-}$ [M= Pd^{II}] prompted us to assume the following assignments.

$^1A_{1g} \longrightarrow {}^1A_{2g}\,[b_{2g}(\pi^*) \longrightarrow b_{1g}(\sigma^*)]$, (d-d):

$^1A_{1g} \longrightarrow {}^1B_{1g}\,[b_{2g}(\pi^*) \longrightarrow a_{1g}(\sigma^*)]$, (d-d); $^1A_{1g} \longrightarrow {}^1E_g\,[e_g(\pi^*) \longrightarrow b_{1g}(\sigma^*)]$, (d-d); $^1A_{1g} \longrightarrow {}^1B_{1u}\,[b_{2g}(\pi^*) \longrightarrow a_{2u}(\pi^*)]$, (C.T) ; $^1A_{1g} \longrightarrow {}^1E_u\,[e_g(\pi^*)] \longrightarrow a_{2u}(\pi^*)]$, (C.T).

The relation between the bands in the present complexes and the described for the typical complexes $[M(CN)_4]^{2-}$ leads to the conclusion that all the new complexes have the same square planer geometry.

NMR spectroscopy

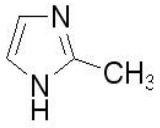
The PMR Spectra of the ligand exhibit signals at δ 2.5 (m, CH_3), 7.0-8.0(ArH), 10.2 (OH) and 12.6 (SH). This shows that the ligands exist in pyrrole form rather than pyrazole form, which support the IR observation and non involvement of proton on the nitrogen in the reaction. The signals at δ 10.2 in spectra of the complex, confirming that the hydroxyl group has reacted with metal (II) moiety via deprotonation. The presence of a singlet at δ 12.6 suggests that in the complex the ligand retains pyrrole form. The signal due to azomethine proton in the complex appears at δ 9.0. The downfield shift observed indicates the deshielding effect due to the coordination of nitrogen to the central metal ion.

Table 1: Solubility of 2- Methyl imidazole in benzene

Temp; ^{0}c b.p., ^{0}c. (760mm.)	Molality
3.2	4.57
16.8	6.07
21.1	6.87
25.4	7.44
29.3	8.24
31.4	8.54

Table 2: Important ir spectral bands and their assignments

Compound	ν (c=o)(cm^{-1})	$\nu_{NH(\beta)(cm\text{-}1)}$	$\nu_{NH(\gamma)(cm\text{-}1)}$	$\nu_{C\ NH2(cm^{-1})}$	Ring(cm-1)
$[Pd(2\text{-METHYLIMIDAZOLE})_2Cl_2]$	1640	1555	845	-	1650



2-METHYL IMIDAZOLE

CONCLUSION

The complexes have anti tumor activity. Filamentous growth in bacteria is indicative of the ability of an agent to react with DNA, giving selective inhibition of DNA synthesis but no accompanying effect on other biosynthetic pathways. Induction of bacteriophage from lysogenic bacteria and mutogenicity of some active complexes are also important evidence for direct DNA attack. Biochemical studies on cells in culture have shown that cis $[PdCl_2(2\text{-methyl imidazole})_2]$ selectively and persistently inhibits the rate of DNA synthesis as compared to RNA and protein synthesis .It is postulated that the primary chemical lesion in the DNA, inhibiting it as a template for replication. Studies on cis and trans isomer of $[PdCl_2(2\text{-methyl imidazole})_2]$ on cells in vitro showed that trans binds to cell macromolecules as effectively as cis . There are more palladium moieties bound per molecule of DNA than to either RNA orbitals protein. Interstand cross-linking has been demonstrated to occur for Pd compounds, but to a much lesser extent than for alkylating agents. The balance of evidence highly favours the proposal that this form of binding to DNA is not an important cytotoxic events . Linking between bases on the same strand has been circulating white Blood cells, although this is lower than that for most other anti tumor drugs. Other side effects include nausea, vomiting, and high frequency hearing loss (ototoxicity). Peripheral neuropathy has been observed on repeated treatment.

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