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Biologically Important Coordination Compounds of Palladium(II) and Platinum(IV) with 2-Substituted Benzimidazole

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Palladium(II) and platinum(IV) chloride react with 2-substituted benzimidazole to give complexes of the formula MLCl where M = Pd(II) and Pt(IV), L = 1,2-bis(2-benzimidazolyl) ethanol (BBIE) and 1,2-bis(2-benzimidazolyl) ethane thiol (BBIET). These complexes have been characterized on the basis of elemental analysis, conductance measurement, IR and NMR studies. The square-planar geometry has been suggested for these complexes. These complexes have been evaluated for their fungicidal activity against *Alternaria alternata* and *Aspergillus niger* by spore germination inhibition method.

Key Words: Pd(II), Pt(IV), Compounds, Benzimidazoles, Biological activity.

INTRODUCTION

The benzimidazole derivatives and their metal complexes have been investigated for their biological activities by many workers[1-4]. Kukalenko *et al.*[5] have reviewed the preparation, structure, stability and their activity towards bacteria, fungi, higher plants and animals. The preparation and characterization of Pd(II) and Pt(IV) complexes of substituted benzimidazole have been reported by few workers[6, 7]. In the present communication we report the preparation and characterization of complexes of Pd(II) and Pt(IV) with 2-substituted benzimidazole, *i.e.*, 1,2-bis(2-benzimidazolyl) ethanol (BBIE) and 1,2-bis(2-benzimidazolyl) ethane thiol (BBIET). They have been characterized on the basis of elemental analysis, conductance measurement, IR, NMR studies. Fungicidal properties of these metal chelates have also been studied and reported in the present communication.

EXPERIMENTAL

All chemicals used were from BDH. The 2-substituted benzimidazole ligand 1,2-bis (2-benzimidazolyl) ethanol (BBIE) and 1,2-bis (2-benzimidazolyl) ethane thiol (BBIET) have been prepared by the method reported in literature[8,9]; m.p.s were determined in open capillaries and are uncorrected. IR spectra (KBr) were recorded on a Perkin-Elmer 577 grating IR spectrophotomer. The ^{1}H NMR spectra (chemical shift in δ ppm) were obtained from FX 90Q JEOL spectrometer at 90 MHz in DMSO-d_6 using TMS as an internal reference. The purity of all the compounds were checked by running TLC on silica gel-G-plates using chloroform-ethyl acetate (1 : 1) mixture and spots were visualized by iodine vapours. The metal contents of the complexes were determined by standard literature procedures. The analytical data and physical properties of complexes are given in Table-1.

TABLE-1
PHYSICAL PROPERTIES AND ANALYTICAL DATA OF METAL COMPLEXES OF 2-SUBSTITUTED BENZIMIDAZOLE DERIVATIVES

Reactants (g)		Mol ratio	Complex	Decomp. temp. (°C)	Elemental analysis (%), Found (Calcd.)					
					C	H	N	Cl	S	M
$C_{16}H_{14}N_4O$ (BBIE)	—	—	—	284	68.86 (69.05)	4.96 (5.07)	19.91 (20.13)	—	—	—
$C_{16}H_{14}N_4s$ (BBIET)	—	—	—	202	64.98 (65.28)	4.70 (4.79)	18.92 (19.03)	—	10.62 (10.89)	—
$H_2PtCl_6 \cdot 6H_2O$ (0.517)	BBIE (0.278)	1 : 1	Pt(BBIE)Cl	286	37.46 (37.83)	2.33 (2.56)	10.90 (11.03)	6.68 (6.99)	—	38.14 (38.42)
$H_2PtCl_6 \cdot 6H_2O$ (0.517)	BBIET (0.294)	1 : 1	Pt(BBIET)Cl	256	36.36 (36.67)	2.39 (2.48)	10.49 (10.69)	6.58 (6.78)	6.02 (6.11)	37.03 (37.24)
$PdCl_2$ ((0.88)	BBIE (1.39)	1 : 1	Pd(BBIE)Cl	267	45.61 (45.71)	2.98 (3.09)	13.21 (13.33)	8.31 (8.45)	—	25.22 (25.33)
$PdCl_2$ ((0.88)	BBIET (1.47)	1 : 1	Pd(BBIET)Cl	293	43.92 (44.03)	2.84 (2.98)	12.72 (12.84)	8.01 (8.14)	7.21 (7.33)	24.32 (24.40)

Preparation of palladium(II) and platinum(IV) complexes of BBIE and BBIET

The chloroplatinic acid and palladium chloride respectively were used for the synthesis of complexes of platinum and palladium. The metal and the ligand were used in 1 : 1 ratio. The chloroplatinic acid dissolves in absolute alcohol easily while palladium choloride was first dissolved in 0.5 mL concentrated hydrochloric acid before preparing its solution in absolute alcohol. To this solution weighed amounts of BBIE and BBIET in 25 mL absolute alcohol were added with constant stirring. The reaction mixture was refluxed for 3–4 h. The solution was concentrated for small volume under reduced pressure, when the desired product got separated.

RESULTS AND DISCUSSION

The complexes obtained were coloured solids and were stable to air and moisture. They decomposed at high (> 250°C) temperatures. These complexes were measured in 10^{-3} M solution in DMF at room temperature. The low values of molar conductance (10–30 $\text{ohm}^{-1}\ \text{cm}^{-2}\ \text{mole}^{-1}$) revealed the non-electrolytic nature of Pd(II) and Pt(IV) complexes.

TABLE 2
FUNGICIDAL SCREENING DATA

Compounds	Average % inhibition of spore germination after 72 h					
	Alternaria alternata (conc. in ppm)			*Aspergillus niger* (conc. in ppm)		
	100	500	1000	100	500	1000
BBIE	34	42	60	33	40	60
BBIET	37	48	62	35	46	62
Pt-BBIE	43	66	68	45	59	76
Pt-BBIET	49	68	81	46	62	79
Pd-BBIE	41	58	67	43	54	69
Pd-BBIET	43	60	70	41	56	68

In the IR spectra of the ligands the broad and strong absorption bands in the region 3130–3040 cm^{-1} and 1420–1410 cm^{-1} have been assigned to ν_{asym}(NH) and δ(NH) vibrations of —NH group of imidazolyl ring of ligands. The absorption bands are observed almost at the same position in the corresponding spectra of complex derivatives. It confirmed the non-involvement and non-deprotonation of this group on complexation with metal atom. The absorption bands due to asymmetric $\nu_{asym}(CH_2)$ and symmetric $\nu_{sym}(CH_2)$ vibrations in the region 2940–2920 and 2870–2850 cm^{-1} could not be located in the spectrum of these ligand derivaties because of the broad band of —NH vibrations of the imidazolyl ring. However, the weak absorption frequencies at 1430–1390 cm^{-1} have been assigned to >C—H bending and deformation vibrations of —CH and —CH_2 group respectively. The broad absorption bands in the region 3450–3400 and 2600–2550 cm^{-1} assigned to alcoholic (—OH)/mercapto (—SH) groups disappear in the IR spectra of complexes of palladium and platinum which indicates the deprotonation of these groups and coordination of O/S atom of the ligand to the metal ions. Further, the appearance of new bands in the region 495–480 cm^{-1} assigned to ν(M—O)/ν(M—S) vibrations clearly indicates the involvement of these functional groups in chelation of ligand molecule with metal atom. The shifts in the frequency due to >C=N stretching vibrations observed to 1620 cm^{-1} in the IR spectra of ligands shifted towards lower wave number (10–15 cm^{-1}) in the spectra of the complexes. It is suggestive of coordination of tertiary nitrogen of imidazolyl nucleus of the ligand molecules with the metal atom. Further it is supported by the appearance of ν(M—N) bands in the region 545–520 cm^{-1} in the spectra of complex derivatives. The occurrence of new absorption bands in the region

315–310 cm^{-1} has been assigned to ν(M—Cl) stretching vibrations.

The ^1H NMR spectra of the complex derivatives are recorded in d_6-DMSO. The proton signal due to —OH/—SH group at δ 10.2–10.4/2.7–2.8 ppm disappeared in the spectra of complex derivatives indicating deprotonation of —OH/—SH group of the ligand and coordination of alcoholic oxygen/thiolic sulphur with metal atom. Aromatic protons were observed as complex multiplet in the region δ 7.0–7.9 ppm. The proton signals due to —CH_2 and —CH are observed in the region δ 2.3–2.5 and δ 3.1–3.3 ppm in the spectra of the ligands BBIE and BBIET. These signals are slightly shifted downfield in the spectra of complexes indicating the deshielding as a result of coordination of the ligand molecule with palladium or platinum atom. Thus on the basis of elemental analysis and the above discussion a square-planar structure can be proposed for the complex derivatives.

The fungicidal activity increases as the concentration increases. Thus it is evident that the concentration plays a vital role in increasing the degree of inhibition. The metal salts have negligible activity against both the fungi, but on complexation with benzimidazole ligands they were found to be active. The enhanced activity of newly synthesized complex derivatives as compared to those of the ligands can possibly be explained on the basis of chelate formation, presence of donor atoms, basicity as well as structural compatibility with molecular nature of toxic moiety. The appearance of enhanced activity may be due to synergistic mechanism, that is, the free ligands are less active but on complexation show more activity in combination with metal ions[11]. In fact the platinum(IV) complexes of the present ligands were found to be more active against both the fungi even at low concentration (100 ppm) in comparison to palladium(II).

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