

PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF 2-METHYLBENZOXAZOLE AND 2-METHYLBENZOTHIAZOLE

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ABSTRACT

Complex compounds of palladium(II) and platinum(II) with 2-methylbenzoxazole (2MeBO=L) and 2-methylbenzothiazole (2MeBT=L'), ML_2X_2 (M = Pd, X = Cl, Br, I, SCN; M = Pt, X = Cl) and $ML_2'X_2$ (M = Pd, X = Cl, Br, I, SCN; M = Pt, X = Cl) have been isolated and characterized by electrical conductivity and IR spectral measurements. 2-Methylbenzoxazole is N-bonded whereas 2-methylbenzothiazole is indicated to be S-coordinated.

INTRODUCTION

THE role of metal ions in promoting the biological functions of various compounds is well established¹. Several complexes of 2-substituted benzoxazoles and their analogues have been found to possess anti-bacterial activity². Platinum metal complexes with various ligands³ including thiazoles⁴ have also been studied for their oncological potentialities. Therefore, the complexes of 2-methylbenzoxazole and 2-methylbenzothiazole with the platinum metals may be expected to be biologically significant. The ligands are also of theoretical interest as the substitution at 2-position may sterically and/or electronically affect the coordination behaviour of heteroatoms at 1- and 3-positions^{5,6}.

Though the coordination behaviour of 2-methylbenzoxazole and 2-methylbenzothiazole towards a number of first row transition metals⁶⁻¹⁰ have been studied, there are few systematic reports of their complexes with heavier metals^{11,12}. We have, therefore, investigated the mode of coordination of these ligands in their palladium(II) and platinum(II) complexes.

EXPERIMENTAL

Materials: 2-Methylbenzoxazole (Fluka), 2-methylbenzothiazole (Kodak), PdCl₂ (Johnson Matthey) and K₂PtCl₄ (Arora Matthey) were used as supplied. Palladium bromide was prepared by dissolving freshly precipitated palladium hydroxide in 48% HBr. The solution was evaporated on water bath and dried over fused CaCl₂.

Preparation of the complexes:

PdL₂Cl₂: An aqueous solution of PdCl₂ (1 mmol) was added to an aqueous suspension of 2-methyl-

benzoxazole (4 mmol). On warming, a light yellow precipitate appeared which was filtered, washed with water, alcohol and ether in succession and dried under IR lamp.

PtL₂Cl₂: This was obtained from K₂PtCl₄ similarly.

PdL₂Br₂: 2-methylbenzoxazole (4 mmol) was suspended in water and treated with an aqueous solution of palladium bromide (1 mmol) containing a little hydrobromic acid and the precipitated complex was isolated as described above.

PdL₂I₂: A solution of PdL₂Cl₂ (1 mmol) in chloroform was added to 2 mmol of KI dissolved in water-alcohol mixture. The dark brown solution obtained was evaporated to dryness on a water bath. The residue was purified by washing successively with hot water, ethanol and ether and dried under IR lamp.

PdL₂(SCN)₂: The solution of Pd(2MeBO)₂Cl₂ (1 mmol) in dichloromethane was added to a solution of KSCN (2 mmol) in ethanol-dichloromethane mixture. The solution turned orange and slowly a precipitate was formed. The mixture was evaporated to dryness to give a pinkish yellow residue which was washed with water to remove KCl and then with alcohol and ether successively. The product was dried under IR lamp.

The 2-methylbenzothiazole complexes, PdL₂Cl₂, PdL₂Br₂, PdL₂(SCN)₂ and PtL₂Cl₂ were prepared analogously to that of the corresponding 2-methylbenzoxazole complexes.

PdL₂I₂: KI (2 mmol) was dissolved in ~1 cm³ water and diluted with ethanol and dichloromethane and a solution of Pd(2MeBT)₂Cl₂ (1 mmol) in dichloromethane was added to it. The brown red solution thus formed was evaporated to dryness and the solid was repeatedly washed with hot water, alcohol and ether and dried under IR lamp.

Analysis of the complexes:

C, H and N were microanalyzed at CDRI, Lucknow. Sulphur and halogens were determined by fusion and precipitation as BaSO₄ and silver halides respectively. Palladium was estimated as palladium dimethylglyoximate and platinum was determined as metal by ignition.

Physical measurements:

Infrared spectra were measured on Perkin Elmer 577 spectrophotometer in the region 200–4000 cm⁻¹

as caesium iodide discs. Electrical conductivity was measured with a Phillips conductivity meter (model PR 9500/90).

RESULTS AND DISCUSSION

The compounds isolated, the data on their elemental analysis and their main infrared bands are listed in tables 1, 2 and 3 respectively. The analytical data in all cases indicate the composition of the complexes to be ML₂X₂. The compounds are too

Table 1 Analytical data and molar conductivities (ΛM) of complexes of 2 MeBO(L) and 2MeBT(L')

Complex	Conductivity ohm ⁻¹ cm ² mole ⁻¹	% Found (Calculated)					
		M	C	H	N	S	X
PdL ₂ Cl ₂	131	24.1 (23.9)	44.0 (43.3)	3.0 (3.1)	6.5 (6.3)	—	15.7 (16.0)
PdL ₂ Br ₂	126.8	19.5 (19.9)	36.4 (36.0)	3.0 (2.6)	5.0 (5.2)	—	30.3 (30.0)
PdL ₂ I ₂	197.3	16.6 (16.9)	30.5 (30.6)	2.5 (2.2)	4.0 (4.4)	—	—
PdL ₂ (SCN) ₂	92.1	21.9 (21.7)	44.5 (44.2)	2.5 (2.8)	11.3 (11.4)	13.3 (13.1)	—
PtL ₂ Cl ₂	116.4	36.3 (36.6)	36.2 (36.0)	2.5 (2.6)	5.1 (5.2)	—	13.5 (13.3)
PdL ₂ Cl ₂	293	22.4 (22.3)	40.0 (40.4)	3.0 (2.9)	5.5 (5.8)	13.3 (13.5)	14.8 (14.9)
PdL ₂ Br ₂	186.2	18.9 (18.7)	33.8 (34.0)	2.5 (2.4)	4.6 (4.9)	11.0 (11.3)	28.0 (28.3)
PdL ₂ I ₂	231.5	15.9 (16.1)	28.6 (29.0)	2.0 (2.1)	4.6 (4.2)	9.3 (9.7)	—
PdL ₂ (SCN) ₂	99.2	19.8 (20.3)	41.2 (41.5)	3.0 (2.6)	10.9 (10.7)	24.5 (24.6)	—
PtL ₂ Cl ₂	86.8	34.3 (34.5)	33.8 (34.0)	2.5 (2.4)	4.6 (4.9)	11.2 (11.3)	12.2 (12.5)

Table 2 Principal IR bands (cm⁻¹) of 2 MeBO(L) and its complexes

L	1615s. sp	1575–1572s. br	923s. sp	—	—
PdL ₂ Cl ₂	1598m. sp	1580s. sp	933w. sp	310m. sp	378s. sp
		1570sh		300sh	330s. sp
PdL ₂ Br ₂	1598m. sp	1580s. sp	933w. sp	310m. sp	262s. sp
		1570sh			
PdL ₂ I ₂	1598m. sp	1580s. sp	935w. sp	318m. sp	228s. sp
		1570sh			
PdL ₂ (SCN) ₂	1600w. sp	1580sh	945w. sp	288m. sp	—
		1562s. sp			
PtL ₂ Cl ₂	1602m. sp	1580sh	940w. sp	310m. sp	335
		1570s. sp		300s. sp	327s. sp
Assignment	Oxazole I	Oxazole II	ν_{C-O}	ν_{M-N}	ν_{M-N}

Table 3 Principal IR bands (cm^{-1}) of 2 MeBT(L') and its complexes

L'	1510– 1495m,mbr	639s, sp	—	—
PdL ₂ Cl ₂	1495m,sp	608m,sp	290m,sp 285sh	365s,sp 320m,sp
PdL ₂ Br ₂	1498m,sp	608m,sp	290m,sp 285sh	270m,sp
PdL ₂ I ₂	1495m,sp	600m,sp	292m,br 275sh	230 225–m,sp
PdL ₂ (SCN) ₂	1495m,mbr	602w,sp	290m,sp	—
PtL ₂ Cl ₂	1495s,mbr	610 598 _{m,triplet}	285m,sp 275sh	355m,sp 322s,sp
Assignment	$\nu_{\text{C=N}}$	$\nu_{\text{C-S}}$	$\nu_{\text{M-S}}$	$\nu_{\text{M-X}}$

insoluble in water and less polar organic solvents like acetone to permit electrical conductivity measurements. Solutions in more coordinating solvents like nitromethane or DMF show high molar conductivity indicating ready solvolysis and only weak coordination of the ligands. Such solvolysis was also observed by Peyronel *et al*¹³ in the 2-methylbenzothiazole complexes.

Infrared spectra:

(a) *2-Methylbenzoxazole complexes*: 2-Methylbenzoxazole shows a sharp and strong band around 1615 cm^{-1} and a slightly broad band at $1575\text{--}72 \text{ cm}^{-1}$ which are assigned as oxazole I and oxazole II bands respectively^{14,15}. A sharp and strong band at 923 cm^{-1} in the ligand is supposed to have significant $\nu_{\text{C-O}}$ contribution^{14,15}. It is generally admitted that when a $-\text{X}-\text{C}=\text{N}-$ group coordinates through the nitrogen atom, the electronic shift $-\text{X}-\text{C}=\text{N}-$ decreases the C=N and increases the X-C character thus exhibiting a negative shift in oxazole bands with a high $\nu_{\text{C=N}}$ contribution and a positive shift heterocyclic ring vibration with a high $\nu_{\text{C-O}}$ contribution¹⁵. We observe that in the palladium and platinum complexes, the oxazole I band shifts to lower wavenumbers ($\sim 15 \text{ cm}^{-1}$), and the oxazole II band is only very slightly affected whereas the heterocyclic ring vibration frequency moves to higher wavenumbers ($10\text{--}20 \text{ cm}^{-1}$). Therefore, the ligand is proposed to be coordinated through the nitrogen atom in these complexes. All the complexes also exhibit sharp bands of medium intensity in the $317\text{--}288 \text{ cm}^{-1}$ region, which are attributable to M-N stretching mode.

(b) *2-Methylbenzothiazole complexes*: 2-Methylbenzothiazole shows bands at 1593, 1572, 1528, 1432

and 1371 cm^{-1} of which 1593, 1572, 1432 and 1371 cm^{-1} bands were not much affected on complexation but the band at 1528 cm^{-1} was found to undergo appreciable shift¹³. We also observed bands at 1590, 1521, 1430 and 1370 cm^{-1} in the spectrum of the ligand and found that only the 1521 cm^{-1} band undergoes a negative shift ($\sim 15 \text{ cm}^{-1}$) in the complexes. The 1521 cm^{-1} band is, therefore, tentatively assigned as due mainly to $\nu_{\text{C=N}}$. In the $\nu_{\text{C-S}}$ region ($720\text{--}500 \text{ cm}^{-1}$) the ligand shows a medium and sharp band at 639 cm^{-1} ascribed to C-S stretching¹³. This band also moves to lower frequency region between $610\text{--}600 \text{ cm}^{-1}$ in all the complexes with slight reduction in intensity. The decrease in $\nu_{\text{C-S}}$ indicates the possibility of coordination through the sulphur atom. Hence, the linkage of the ligand is proposed through sulphur. This is justified in view of the following argument. The coordination through sulphur will generate a positive centre at the sulphur atom and this, in turn, will reduce the possibility of delocalization thereby encouraging the flow of electrons from the C=N towards sulphur. This implies a reduction in C=N bond order and the consequent shift in the $\nu_{\text{C=N}}$ to lower wavenumber. The general opinion that benzothiazoles always bind through nitrogen has been questioned^{11,16}. Shul'man and coworkers¹¹ showed M-S bonding in the benzothiazole complexes on the basis of X-ray spectral emission studies. Dash and Rao¹⁶ also suggested M-S bonding in the Ag(I) complexes of benzothiazole and 2-methylbenzothiazole on the basis of infrared evidences. Bonding through the sulphur atom in the Pd(II) and Pt(II) complexes is also indicated by the appearance of a band in $292\text{--}285 \text{ cm}^{-1}$ region which can be ascribed as $\nu_{\text{M-S}}$.

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NEWS

THINKING THROUGH THE NOSE

...“Breathe through your nose—in, out, in, out. Hold a mirror in front of your nostrils. You'll find the pools of condensation from your two nostrils are different in size. Peculiar, isn't it? At any given moment you see with both eyes, hear with both ears, yet breathe mainly through one nostril. This dominance lasts anywhere from one hour to more than three hours, then reverses over a period of minutes. The yogis of ancient India first discovered this subtle rhythm and its mental correlates more than 5,000 years ago—though the 'nasal cycle' itself wasn't documented in the West until the late 19th Century.... My colleagues—Floyd Bloom of the Scripps Clinic & Research Foundation in La Jolla, California, and Deborah Werntz of U. California, San Diego—and I...investigated a supposed relationship between the nasal cycle and a rhythm in brain hemisphere dominance.... It seems that the hemispheres alternate in a steady rhythm. On the average, our dominant mode of thinking shifts from left to

right hemisphere and back again about 10 times every 24 hours. That means you may have more luck balancing a checkbook during an episode of left-brain dominance and enjoy the arts more when your right brain is 'on.' Our studies show that you can tell which side of the brain is dominant at any given time. You just test which nostril you're using most. Right-nostril dominance goes with left-brain activity, left-nostril with the right brain. But beyond that, by forcing a switch in your breathing you can actually stimulate the less active hemisphere. A person breathing through the right nostril can activate the right hemisphere simply by forcing air through the left nostril, and vice versa.”

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