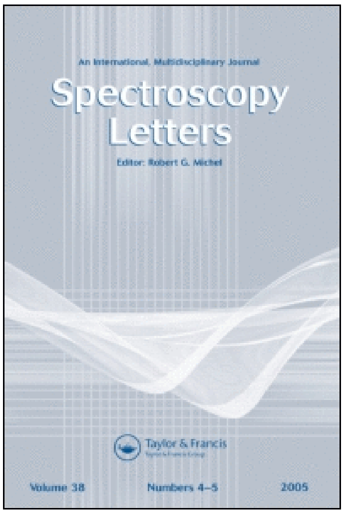

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Spectral Studies of Some Pyridine and Bipyridine Complexes of Platinum(II)

Badri Vishal Agarwala[a]
[a] Chemical Laboratories, University of Allahabad, Allahabad, India

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SPECTRAL STUDIES OF SOME PYRIDINE AND BIPYRIDINE COMPLEXES OF PLATINUM(II)

Badri Vishal Agarwala
Chemical Laboratories, University of Allahabad
Allahabad 211002, India.

Introduction

The increasing importance of complexes of platunum(II) owing to their potential use as antitumour drugs has aroused interest[1]. Coordination compounds formed by nitrogen donor ligands have been found to be significant in this context. Some of the important cis-platinammine active antitumour drugs bind covalently to DNA under specific conditions, whereas the inactive trans- compound does not. Spectral studies of dichloro(2,2'-bipyridine)platinum(II)[2], cis- and trans-dichloro(dipyridine)platinum(II)[3] have been undertaken anticipating that these platinum(II) compounds in coordination with a base would provide additional evidence on the electronic configuration of such complexes. cis-Pt(py)$_2$Cl$_2$ has recently been found to be of biochemical importance and its antitumour and antimitogenic properties have been reported[4-6]. It is less toxic to mice and increases the survival time of mice affected by tumour. Pfeffer[7] has studied the i.r. and Raman spectra of cis- and trans-Pt(py)$_2$Cl$_2$ and coordinate bonding property has also been probed by X-ray studies[8-9]. Substitution[10] and redox reactions of $Pt(bipy)Cl_2$ have also been investigated[11-12]. ESCA studies and its correlation with nuclear quadrupole resonance[13] and solvent effects[14] on its electronic spectra has also been reported.

In the present investigation, magnetic circular dichroism along with electronic absorption spectra have been described. NMR and magnetic studies have in addition been recorded for these complexes of platinum to further elucidate their configuration. The bipyridine complex of platinum has been studied in several solvents due to its fair solubility and the solvent effect has been discussed. The shift in absorption band with an increase in the proton-donating power of solvent was reported earlier for the complex cis-$[Fe(bipy)_2(CN)_2]$.[15]

Experimental

K_2PtCl_4 was obtained from Wako Pure Chemical Industries Ltd.,Japan. Freshly distilled pyridine and other solvents were used. Complexes were prepared according to literature methods[2,3] and checked by elemental analysis.

Anal. Found: C, 28.09; H, 1.79; N, 6.58; Cl, 16.77%, calcd. for $C_{10}H_8Cl_2N_2Pt$: C, 28.44; H, 1.91; N, 6.6; Cl, 16.8%. Found (cis-): C, 28.37; H, 2.28; N, 6.75; Cl, 16.28%. Calcd. for $C_{10}H_{10}Cl_2N_2Pt$ (cis- & trans-): C, 28.30; H, 2.37; N, 6.60; Cl, 16.73%. Found (trans-): C, 28.01; H, 2.35; N, 6.56; Cl, 17.14%.

Electronic absorption spectra was recorded on a Shimadzu automatic recording spectrophotometer model MPS-50. MCD spectra was obtained on a JASCO ORD/UV-5 spectrometer with its electromagnet. NMR spectra was taken on a 100 MHz JEOL spectrometer using TMS as standard. Gouy's balance was used for magnetic susceptibility measurements at room temperature.

Results and Discussion

The electronic absorption spectra of cis- and trans-$Pt(py)_2Cl_2$ were recorded in chloroform as well as in KBr disc. Weak absorption band arising from d-d transition is observed for the feebly coloured complex in the visible region at 27,000 cm^{-1} ($\epsilon = 45$) and five absorption bands in the ultraviolet region for the trans- compound (Table 1). Pyridine itself shows vibrational bands [16] at about 40,820, 39,525, 38,910 and 38,020 cm^{-1}, hence the absorption bands appear due to obvious reasons.

In the cis- compound, the weak d-d band is shifted to 34,200 cm^{-1} and also in MCD spectra. Absorption band at 38,000 cm^{-1} may be assigned to a $\pi - \pi^*$ transition of pyridine

Table 1. Absorption maxima of cis- and trans-$Pt(py)_2Cl_2$ in $CHCl_3$ and MCD data

cis-$Pt(py)_2Cl_2$		trans-$Pt(py)_2Cl_2$	
Absorption spectra (kk) $CHCl_3$	MCD(kk)	Abs. sp.(kk) $CHCl_3$	MCD(kk)
34.2	32.0	33.4 sh	28.3
38.6		35.7	30.6
		37.0	32.3
		38.0	36.0
		38.7	37.5
		27.0	

in favour to CT band. An absorption band observed in solid state spectra at 38,400 cm^{-1} arises of the same transition. It may be postulated that the expected $n-\pi^*$ transition due the presence of a lone pair of electrons in nitrogen atom of the pyridine molecule submerged under the $\pi-\pi^*$ transition.

From studies of absorption spectra in various solvents the maxima of electronic absorption and MCD extrema were obtained (Table 2)

Band 1 is assigned to a MLCT in preference to d-d band because of normal dispersion of MCD spectra which agrees with earlier work[14]. The extinction coefficient of this band (ca. 3500 $l.mol^{-1}cm^{-1}$) is also consistent with such an assignment. Vibrational fine structure for band 2 is observed in the u.v. region due to $\pi-\pi^*$ transition of coordinated bipyridine. This assignment is in agreement with the MCD spectrum, which is positive in this region. Similar observations have been made on luminescence studies of tris(bipyridine)rhodium(III) ion[17]. Band 3 shows strong solvent effect and it shifts from 33.4 kk in DCB to 36.6

Table II. Solvent effects on the electronic absorption spectra of the complex $Pt(bipy)Cl_2$

Solvent	Band 1	Band 2	Band 3	Band 4
		ν_{max}/kk		
1. Chloroform	25.0,26.3 sh	30.8,32.0	35.1	39.2
2. Methanol	26.5	31.1,32.2	36.6	39.8
3. Dimethylsulphoxide (DMSO)	26.0	30.6,31.7	36.0 sh	Solvent absorbs
4. 1,1,2,2-Tetrachloroethane (TCE)	25.3	30.8,31.9	35.0	''
5. o-Dichlorobenzene (DCB)	24.2	30.5,31.7	33.4	''
6. N,N-Dimethylformamide (DMF)	25.8	30.6,31.8	35.7	''

Table III. Solvent effects on magnetic circular dichroism spectra of the complex Pt(bipy)Cl_2

Solvent	kK		
1. Chloroform	23.5	30.5,34.0	38.0,39.5
2. Methanol	22.5	30.8,35.4	39.5
3. Dimethylsulphoxide	24.7	29.0,30.5	37.0
4. 1,1,2,2-Tetrachloroethane	24.0	26.8,28.3	30.7,34.3
5. o-Dichlobenzene	23.0	29.8	
6. N,N-Dimethylformamide	24.5	30.3	34.5

in MeOH (3.2 kk). Band 3 is again assigned to MLCT band because of normal MCD dispersion at 35,400 cm^{-1}. Band 4 could not be observed in solvents DMSO, TCE, DCB and DMF due to strong absorption in higher wavenumbers. However, band 4 observed in $CHCl_3$ is reasonably assigned to $\pi - \pi^*$ transition of bipyridine , as suggested by Rossiello and Furlani[18] which is true for MeOH medium as well. The presence of o-, m- and p-protons of pyridine were indicated by ^{1}H-NMR spectra in the trans- compound. All the platinum(II) complexes were found to be diamagnetic which is in conformity with their square planar arrangement.

Summary

Electronic absorption spectra and magnetic circular dichroism of three square planar Pt(II) complexes , cis- and trans-Pt$(py)_2Cl_2$ and Pt(bipy)Cl_2 have been described. Detailed studies have been carried out for Pt(bipy)Cl_2 due to its fair solubility in many solvents and the solvent effect on its electronic spectra is investigated. The band assignments of the electronic spectra are discussed which are supported by MCD spectrum.

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