

## Synthesis and spectral studies of zinc(II) and palladium(II) complexes of amide ligands derived from 2-aminopyridine

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A few complexes of Zn(II) and Pd(II) with N-(2-pyridyl)-3-carboxypropanamide and N-(2-pyridyl)-2-carboxybenzamide derived from 2-aminopyridine have been prepared and characterised on the basis of elemental analysis, conductivity measurements, thermal and spectral (IR,  $^1\text{H}$  NMR, UV/vis) studies. Molar conductivities indicate non-electrolytic behaviour of most of the complexes. Spectral studies show the coordination of Zn(II) through amide oxygen and pyridine nitrogen atom, while in case of Pd(II), pyridine nitrogen atom alone coordinates. On the basis of these studies, probable structures of the complexes have been assigned.

The coordination behaviour of amide ligands is of significance in case of a number of current chemical problems<sup>1-6</sup>. The knowledge of metal ion interactions with the amide group will provide insight into protein structure and functional pathways in biological system. Zinc(II) metal ion has an important biological role in enzyme system of animals and plants<sup>7,8</sup>, whereas Pd(II) coordinates differently with interesting site in amide ligands<sup>1</sup>.

In this note, we report the synthesis and spectral studies of Zn(II) and Pd(II) complexes of amide ligands derived from 2-aminopyridine.

### Experimental

All the chemicals were of AR grade and were used without further purification.

#### Preparation of the ligands

The ligands N-(2-pyridyl)-3-carboxypropanamide (PCPA) and N-(2-pyridyl)-2-carboxybenzamide (PCBA) were prepared from 2-aminopyridine using the general method of Nonoyama *et al.*<sup>9</sup> with slight modifications and have been reported elsewhere<sup>10-12</sup>.

#### Preparation of the complexes

In a typical preparation, the ligand (2 mmol) was suspended in dry methanol/ethanol and 1 mmol methanolic solution of metal salts (zinc acetate,

palladium chloride) were added to it dropwise. A clear solution thus obtained was stirred for 45 min. A white precipitate formed, was filtered, washed with methanol/ethanol and dried *in vacuo* over  $\text{P}_4\text{O}_{10}$ .

The elemental analysis were carried out using Perkin Elmer CHN analyser, whereas the metal contents were determined by atomic absorption spectroscopy after digesting the complexes with conc  $\text{HNO}_3$ . The IR spectra were recorded on a Perkin Elmer 1710 and 598 FT spectrometer in a direct film in Nujol mulls and CsI. The electronic spectra were recorded in DMF on a Beckman DU-64 UV/vis spectrophotometer. The  $^1\text{H}$  NMR spectra were recorded at ambient temperature on BRUKER AC 200 MHz NMR spectrophotometer. Molar conductivities were measured in DMF ( $10^{-3}$  M), with a systronic digital conductivity meter model 304. Thermal analysis was done on Rigaku 8150 thermoanalyser at a heating rate of  $10^\circ\text{C min}^{-1}$  and chart speed was maintained at  $2.5 \text{ mm min}^{-1}$ . A platinum crucible was used with alumina as the reference material.

### Results and discussion

The characterization data of the complexes are presented in Table 1. All the isolated complexes were found to be white (light yellow) microcrystalline or powder-like solids. They were all non-hydroscopic except  $\text{Zn}(\text{PCBA})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  and insoluble in water and most of the organic solvents, but were freely soluble in DMF and DMSO. The values of most of the complexes in DMF indicated these to be in good agreement with non-electrolytic nature (with partial dissociation)<sup>13</sup>.

All the complexes were found to decompose at higher temperature ( $\sim 220^\circ\text{C}$ ). The decomposition temperature of the complexes obtained from their thermograms are recorded in Table 1. The thermograms of  $\text{Zn}(\text{PCBA})_2(\text{H}_2\text{O})_2 \cdot (\text{OAc})_2$  and  $\text{Zn}(\text{PCPA})_2(\text{H}_2\text{O})_2 \cdot (\text{OAc})_2$  show initial mass loss in the temperature range  $160-180^\circ\text{C}$  corresponding to loss of two water molecules. The expulsion of water molecules in this range of temperatures indicates that the water molecules are coordinated<sup>14</sup>. The presence of water molecules in these complexes is further evidenced by their DTA curves which give endothermic peaks in the temperature range  $150-200^\circ\text{C}$ . One of the complexes of Zn(II) i.e.  $\text{Zn}(\text{PCBA})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  gives initial mass loss

Table 1—Characterization data of the complexes

Complex	Found (Calcd), %				$\Lambda_M$ $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$	Decomp. Temp. (°C)	$\lambda_{\text{max}}$ (nm)
	C	H	N	M			
Zn(PCPA) <sub>2</sub> Cl <sub>2</sub>	40.84 (41.22)	3.78 (3.82)	10.82 (10.68)	11.34 (12.40)	32	225-420	280
Zn(PCPA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	37.04 (37.43)	3.26 (3.47)	9.28 (9.70)	11.01 (11.27)	28	230-410	283
Zn(PCBA) <sub>2</sub> Cl <sub>2</sub>	48.97 (50.32)	3.21 (3.23)	12.08 (13.54)	10.32 (10.48)	30	222-412	286
Zn(PCBA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O	45.16 (45.15)	3.14 (3.18)	11.96 (12.16)	9.22 (9.41)	33	210-388	287
Zn(PCPA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ·(OAc) <sub>2</sub>	43.28 (43.49)	3.94 (3.95)	9.20 (9.23)	10.25 (10.71)	133	205-432	283
Zn(PCBA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ·(OAc) <sub>2</sub>	50.86 (51.21)	3.27 (3.41)	7.94 (7.97)	9.02 (9.25)	136	220-408	287
Pd(PCPA) <sub>2</sub> Cl <sub>2</sub>	38.23 (38.42)	3.54 (3.56)	9.91 (9.94)	18.76 (18.84)	—	210-360	285 412
Pd(PCBA) <sub>2</sub> Cl <sub>2</sub>	43.57 (43.88)	3.02 (3.24)	8.47 (8.56)	16.04 (16.32)	—	202-378	280 409

curve in the temperature range 80-160°C, which indicates that water molecule is present as lattice held water<sup>14</sup>. Also, the DTA peak in the range 100-120°C further gives evidence of the presence of water molecule.

The IR spectra of the ligands have a medium intensity band in the 3170-3140  $\text{cm}^{-1}$  region ( $\nu\text{N}-\text{N}$  stretching band), which shifts to higher frequency indicating non-participation of the nitrogen atom upon coordination<sup>15</sup>. The spectra of the complexes **4**, **5** and **6** also display a band at  $\sim 3400\text{ cm}^{-1}$  which reveals the presence of water in these complexes.

The C=O and C-O stretching frequencies in *ca.* 1535 and 1378  $\text{cm}^{-1}$  in uncomplexed ligands are assigned to  $\nu(\text{COO}^-)_{\text{asym}}$  and  $\nu(\text{COO}^-)_{\text{sym}}$  modes and there is not considerable shift of these in the complexes<sup>15</sup>.

A strong band at 1690  $\text{cm}^{-1}$  due to  $\nu\text{C}=\text{O}$  (amide-I band) in uncomplexed ligands shift ( $\sim 20\text{ cm}^{-1}$ ) to lower frequency in complexes indicating metal coordination of amide  $>\text{C}=\text{O}$  group<sup>15</sup>. Such a low frequency shift of  $\nu\text{C}=\text{O}$  is a good qualitative diagnostic test for the coordination of amide oxygen to a metal centre<sup>10</sup>.

For Pd(PCPA)<sub>2</sub>Cl<sub>2</sub> and Pd(PCBA)<sub>2</sub>Cl<sub>2</sub>, the amide-I band shifted slightly to a higher frequency ( $\sim 5\text{ cm}^{-1}$ ) while the other bands (due to amide group) remained almost in the same positions indicating the non-coordination of the amide group.

All the complexes exhibit a sharp maximum in the 1610-1590  $\text{cm}^{-1}$  region which is attributed to couple stretching mode of the pyridyl C-C and C-N bands<sup>15</sup> which give rise to small frequency shifts and a marked

intensity increase on coordination of the pyridyl N-atom in Zn(II) complexes. Regarding  $\nu(\text{M}-\text{X})$  bands, Zn(II) complexes of PCPA and PCBA show strong bands at 490-470 and 350-400  $\text{cm}^{-1}$  respectively, which can be tentatively assigned to  $\nu\text{Zn}-\text{N}$  and  $\nu\text{Zn}-\text{O}$  bands<sup>15</sup>. The other low frequency bands at  $\sim 310$  and  $\sim 270\text{ cm}^{-1}$  in the zinc(II) complexes are assigned to  $\nu\text{Zn}-\text{NO}_3$  and Zn-Cl respectively<sup>15</sup>. For Pd(II) complexes,  $\nu\text{Pd}-\text{Cl}$  band occurred at 345  $\text{cm}^{-1}$ . Thus, palladium complexes seem to be square-planar coordinated through the pyridine-nitrogen atom alone.

The electronic spectra of zinc(II) complexes show a band at *ca.* 284 nm due to  $\pi-\pi^*$  transitions. In the ligands, this band was observed at *ca.* 297. This hypsochromic shift in the complexes may be due to the donation of lone pair of electrons by the oxygen of the amide group to the central metal atom<sup>16</sup>. The absence of *d-d* transition rules out the presence of any unpaired electron in the zinc ion with electronic configuration  $(n-1)d^{10}, ns^0$  (ref. 17).

The palladium(II) complexes are expected to exhibit three bands at *ca.* 15,000, 20,000 and 25,000  $\text{cm}^{-1}$  due to  ${}^1A_{2g} \leftarrow {}^1A_{1g}$ ,  ${}^1B_{1g} \leftarrow {}^1A_{1g}$  and  ${}^1E_{1g} \leftarrow {}^1A_{1g}$  transitions respectively. But only two bands are observed at *ca.* 24345  $\text{cm}^{-1}$  ( ${}^1E_{1g} \leftarrow {}^1A_{1g}$ ) and 35165  $\text{cm}^{-1}$  (charge-transfer band) for palladium(II) complexes.

The spectrum of PCPA shows four groups of peaks while PCBA shows five groups of peaks between  $\delta$  8.40 and 7.10 ppm (ring protons) and a broad singlet at  $\sim 10.50$  ppm ( $[-\text{COOH}]$  proton), which involve in

hydrogen bonding with the water content of the solvent and amide proton<sup>18</sup>.

In the spectra of the complexes, the signals of the pyridyl H-6 proton shift downfield compared to those of the ligands, suggesting that the pyridine-N atom of the 2-aminopyridine unit is coordinated to the metal ions<sup>19</sup>. As expected, the pyridyl H-3 proton registers a significant upfield shift since it is no longer shielded by the carbonyl group in the *trans*-conformation of the complexed ligands<sup>20</sup>. The magnitude of the shift is comparable to that observed for the zinc complex of NPA<sup>19</sup>.

The upfield shift of carboxylic protons in PCBA complexes may be due to intermediate rate of intermolecular exchange of protons between the carboxylic group and water content in the solvent<sup>18</sup>.

On the basis of the studies carried out, a *trans*-octahedral structure for the zinc(II) complexes and a square planar structure for palladium(II) complexes have been proposed. As indicated by <sup>1</sup>H NMR and IR spectral studies, zinc(II) is coordinated to amide oxygen and pyridine nitrogen having an octahedral geometry with two axial positions occupied by X (X = Cl<sup>-</sup>, H<sub>2</sub>O, NO<sub>3</sub><sup>-</sup>). In case of palladium, only pyridine nitrogen atom coordinates, the two ligands being mutually in the *trans* positions.

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