

## Structural studies of metal complexes containing amide ligands

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**Abstract.** Complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Pd(II) with di-N-phenyl pyromellitic diimide (PhPMDI) and di-N-pyridyl pyromellitic diimide (PyPMDI) were prepared and characterized based on analytical, molar conductance, magnetic, IR, PMR, electronic and ESR data. Based on analytical and molar conductance, the complexes have been formulated as  $[M(\text{PhPMDA})(\text{H}_2\text{O})_2]_n$  ( $M = \text{Mn, Fe, Co, Ni}$ ),  $[\text{Cu}(\text{PhPMDA})]_n$ ,  $[\text{Pd}_2(\text{PhPMDA})\text{Cl}_2(\text{H}_2\text{O})_2]$ ,  $[M(\text{PyPMDA})]_n$  ( $M = \text{Mn, Fe, Co, Ni and Cu}$ ) and  $[\text{Pd}_2(\text{PyPMDA})\text{Cl}_2]$ . In all these complexes PhPMDA acts as a mononegative bidentate ligand whereas PyPMDA acts as a mononegative tridentate one in the form of amide rather than imide. The geometries of the complexes have been proposed based on the electronic spectra. The various bonding parameters have been calculated from the ESR spectra of Cu(II) complexes.

**Keywords.** Amide ligands; metal-amide interactions; polynuclear complexes.

### 1. Introduction

As a part of our systematic investigations on the metal–amide interactions (Ravinder *et al* 1984, 1985), we report here the preparation and characterisation of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Pd(II) complexes with di-N-phenyl pyromellitic diimide (PhPMDI) and di-N-pyridyl pyromellitic diimide (PyPMDI). We have selected ligands which are able to chelate in a bridged manner and form bi/poly nuclear complexes.

### 2. Materials and methods

#### 2.1 Materials

All the chemicals used were of AR grade. The 1,2,4,5-benzene tetracarboxylic anhydride (BTCA) was obtained from Aldrich Chemical Company (USA) and was used as such for the preparation of ligands.

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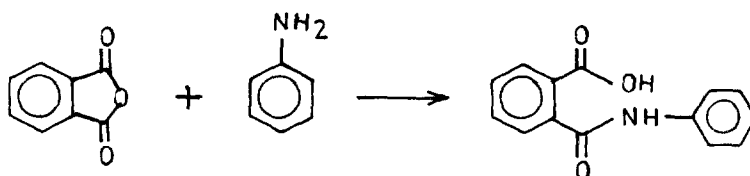
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## 2.2 Preparation of the ligands

2.2a *Preparation of di-N-phenyl pyromellitic diimide (PhPMDI)*: BTCA (0.1 mol) was dissolved in ether, and to this aniline (0.2 mol) taken in ether was added dropwise with constant stirring. The white solid that separated was filtered and washed thoroughly with methanol and the purity of the compound was checked by TLC in 3:1 benzene-methanol system.

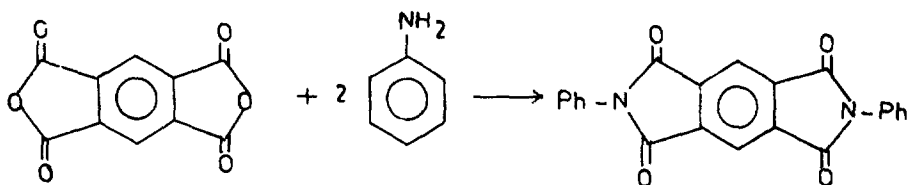
2.2b *Preparation of di-N-pyridyl pyromellitic diimide (PyPMDI)*: BTCA (0.1 mol) dissolved in ether was added dropwise to 2-amino pyridine (0.2 mol) taken in ether with constant stirring. The white solid that separated was filtered and washed thoroughly with ether. The solid product was recrystallized from methanol and the purity of the compound was checked by TLC in 3:1 benzene-methanol system.

The condensation of anhydride with amine does normally lead to the isolation of the corresponding amide compound. The earlier publications (Ravinder *et al* 1984) from our laboratories show that the condensation of phthalic anhydride with aniline also yields the amide compound (scheme 1).



Scheme 1.

In the present investigation the condensation reaction is carried out at room temperature and also between 0°C and -3°C but we have always obtained the imide rather than the amide compound (scheme 2).



Scheme 2.

The above compounds have been characterized by analytical data and by IR, PMR and mass spectral data (data are included in respective tables).

## 2.3 Preparation of the complexes

All the complexes were prepared by mixing an aqueous methanolic solution of metal salts with a methanolic solution of the ligands in 1:2 molar ratio and heating the mixture on a hot-water bath for about 30 minutes. The crystalline complexes formed were suction filtered, washed with hot water and methanol and dried *in vacuo* over anhydrous calcium chloride.

## 2.4 Physical measurements

The analytical data of C, H and N were obtained from the Regional Sophisticated Instrumentation Centre, Chandigarh. Metal content in the complexes was determined either by the volumetric or the gravimetric method. The magnetic susceptibility of the complexes was measured by the Gouy method using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as calibrant. A vibrating sample magnetometer at RSIC, Indian Institute of Technology, Madras, was also employed for the above purpose, when only small amounts of complexes were available. The thermal data of the complexes were obtained using a station thermobalance available at the Indian Institute of Chemical Technology, Hyderabad. The IR spectra of the ligands and the complexes ( $4000\text{--}200\text{ cm}^{-1}$ ) in Nujol mulls or as KBr pellets (using cesium iodate plates in the FIR region) were recorded on a Perkin Elmer-283 spectrometer. The electronic spectra of the Pd(II) complexes in DMF were obtained using a Shimadzu MPS-5000 spectrophotometer. Diffuse powder reflectance spectra of all other complexes were recorded using a Beckman Model DV quartz spectrophotometer. ESR spectra of the Cu(II) complexes in the solid state were recorded at room temperature employing JEOL PE 3X model spectrometer. Mass spectra of ligands were recorded using a varian MAT CH-7 instrument at 70 eV.

## 3. Results and discussion

Analytical and other physical data are given in table 1. The analytical data suggest that all the metal complexes have 1:1 stoichiometry except Pd(II) complexes where the metal to ligand ratio is 2:1. Some of the complexes also contain water and chlorine molecules. Conductance measurements of all complexes other than Pd(II) were not obtained due to poor solubility in all the solvents. However the data on Pd(II) complexes which are soluble in DMSO and DMF, are in accord with their being formulated as non-electrolytes (Geary 1971). The molecular weights of Pd(II) complexes recorded by the Knauer vapour pressure osmometer are shown in table 1. The insolubility of other complexes has restricted the determination of their molecular weights.

### 3.1 Thermal analysis

The decomposition temperatures of the complexes obtained from their thermograms are recorded in table 1. The TGA values of all the complexes of PhPMDA except the complex of Cu(II) show weight loss in the temperature range  $160\text{--}240^\circ\text{C}$  corresponding to two water molecules. The expulsion of water from the complexes in the above temperature range indicates that they are present inside the coordination sphere (Nikolaev *et al* 1969). The presence of water molecules in these complexes is further evidenced by their DTA curves. The Cu(II) complex of PhPMDA and all other metal complexes of PyPMDA are thermally stable upto  $340^\circ\text{C}$  indicating that they are not hydrated. This is also confirmed by the absence of an endothermic peak in the temperature range  $150\text{--}230^\circ\text{C}$  in their DTA curves. All the complexes show only one step transformation at the temperature  $340^\circ\text{C}$  corresponding to loss of the ligand moiety.

**Table 1.** Colours, decomposition temperatures, analytical results and conductivity measurements.

Compound	Colour	Decomp. temp (°C)	Elemental analyses: found (Calc.)%				
			M	C	H	N	$\mu_{\text{eff}}$
PhPMDI <sup>a</sup>	White	> 300	—	71.1 (71.7)	3.2 (3.3)	7.3 (7.6)	—
Na salt of PhPMDA	White	—	—	57.5 (58.9)	2.9 (3.1)	5.7 (6.2)	—
[Mn(PhPMDA)(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Gray	345	11.0 (11.1)	52.9 (53.5)	3.0 (3.6)	5.0 (5.6)	5.9 (6.1)
[Fe(PhPMDA)(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Light yellow	360	11.1 (11.3)	53.5 (54.0)	3.2 (3.6)	5.6 (5.7)	5.5 (5.6)
[Co(PhPMDA)(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Light pink	350	11.5 (11.9)	52.6 (53.1)	3.5 (3.6)	5.7 (5.6)	4.9 (5.0)
[Ni(PhPMDA)(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Pale green	355	11.3 (11.8)	53.0 (53.2)	3.6 (3.6)	5.2 (5.6)	3.2 (3.1)
[Cu(PhPMDA)] <sub>n</sub>	Pale blue	370	13.0 (13.6)	56.0 (56.7)	2.5 (3.0)	5.7 (6.0)	1.83 (1.82)
[Pd <sub>2</sub> (PhPMDA)Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>b-d</sup>	Yellow	350	29.0 (29.5)	36.0 (36.5)	2.0 (2.5)	3.5 (3.9)	—
PyPMDI <sup>a</sup>	White	> 315	—	64.3 (64.8)	2.6 (2.7)	14.9 (15.1)	—
Na salt of PyPMDA	White	—	—	53.0 (53.3)	2.5 (2.6)	12.0 (12.4)	—
[Mn(PyPMDA)] <sub>n</sub>	Ash	350	11.5 (11.9)	52.6 (52.2)	2.5 (2.6)	12.1 (12.2)	5.9 (6.0)
[Fe(PyPMDA)] <sub>n</sub>	Light yellow	365	11.5 (12.1)	52.0 (52.1)	2.5 (2.8)	12.0 (12.2)	5.4 (5.5)
[Co(PyPMDA)] <sub>n</sub>	Dark pink	360	12.5 (12.7)	51.0 (51.8)	2.0 (2.5)	12.1 (12.7)	5.0 (5.1)
[Ni(PyPMDA)] <sub>n</sub>	Light yellow	370	12.3 (12.6)	51.6 (51.8)	2.4 (2.6)	12.0 (12.5)	3.2 (3.1)
[Cu(PyPMDA)] <sub>n</sub>	Pale blue	375	13.3 (13.5)	51.0 (51.3)	2.3 (2.5)	11.8 (12.5)	1.8 (1.8)
[Pd <sub>2</sub> (PyPMDA)Cl <sub>2</sub> ] <sup>b,cd</sup>	Yellow	360	30.5 (30.9)	33.9 (34.8)	1.6 (1.7)	7.7 (8.1)	—

<sup>a</sup> Mass spectrum;  $m/e$  (base peak) 93.0<sup>\*</sup>; <sup>b</sup> Cl 9.83(9.89); 10.27(10.32); <sup>c</sup> Conductivity value = 8.5 and 10.0; <sup>d</sup> Molecular weight = 721.84, 687.84(667.00); <sup>\*</sup> Molecular weight 368 and  $m/e$  (base peak) 174.0; molecular weight 370

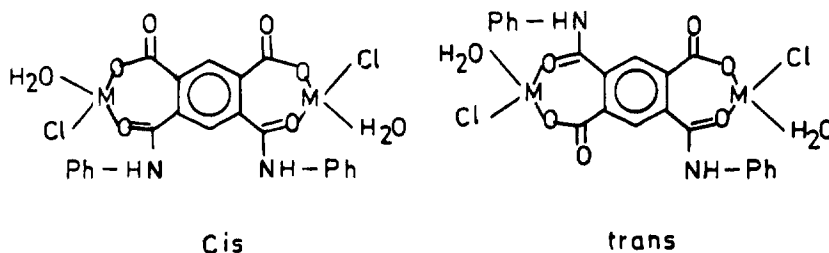
### 3.2 IR spectra

The absence of  $\nu(\text{N-H})$ ,  $\nu(\text{C=O})_{\text{acid}}$  and  $\delta(\text{OH})_{\text{acid}}$  bands in the IR spectra of PHPMDI and PyPMDI implies that the ligands are in the imide form, which was confirmed by <sup>1</sup>H-NMR and mass spectra. The IR spectra of sodium salts of the ligands show bands at 3360, 1660 and 1560  $\text{cm}^{-1}$  corresponding to  $\nu(\text{N-H})$ ,  $\nu(\text{C=O})_{\text{acid}}$  and  $\nu(\text{COO}^-)$  respectively. No change in the  $\nu(\text{N-H})$  band in the complexes suggests the non-involvement of amide nitrogen in coordination (Pannu and Chopra 1974). A downward shift of the  $\nu(\text{C=O})$  band by 30  $\text{cm}^{-1}$  in the complexes suggests the participation of the oxygen of the amide group in complexation (Nakamoto 1978; Mohan et al 1987). The different  $\Delta$ , between the stretching frequencies  $\nu(\text{COO}^-)_{\text{symmetric}}$  and  $\nu(\text{COO}^-)_{\text{asymmetric}}$  in all the metal complexes is greater when compared to the

sodium salt of the ligands indicating the involvement of the oxygen of the carboxylate ion as a monodentate ligand in complexation (Deacon *et al* 1985). The band observed at  $1600\text{ cm}^{-1}$  in the IR spectra of PyPMDA is assigned to the pyridine group and shifted downward by  $40\text{ cm}^{-1}$  in complexes indicating the participation of the nitrogen of the pyridine ring in the metal–ligand bond. An upward shift in in-plane and out-of-plane deformation bands of pyridine ring further confirms the above statement (Dissouky *et al* 1986). The presence of new bands in the range  $880\text{--}650\text{ cm}^{-1}$  in PyPMDA complexes are assignable to coordinated water (Gelfand *et al* 1980) which is absent in the PyPMDA complexes. FIR spectra of metal complex show bands corresponding to  $\nu(\text{M-O})$ ,  $\nu(\text{M-N})$  and  $\nu(\text{M-Cl})$  vibrations (Noboru and Nakamoto 1971; Bora *et al* 1986).

### 3.3 $^1\text{H-NMR}$ spectra

The  $^1\text{H-NMR}$  spectra of PhPMDI and PyPMDI and their palladium(II) complexes are recorded in  $d_6$ -DMSO. The spectra of the PhPMDI and PyPMDI ligands show no resonance signals in the range 3–6.5 ppm due to the amide (N–H) and 9–12 ppm due to the carboxylic (COOH) protons implying that the ligands are in the imide form. Two sets of aromatic multiplets have been assigned for both the ligands. In these ligands the two protons on the central benzene ring appear as only one multiplet in the region 6.5–6.9  $\delta$  and the phenyl or pyridyl protons are present as a big multiplet in the region 6.7–8.2  $\delta$ . If the ligand is symmetrical with *trans* configuration we should obtain a single multiplet for the central benzene ring protons in the complex. If it is in the *cis* configuration we should get two multiplets for these protons. In fact, in the Pd(II) complexes these two protons give only one multiplet at 6.5–7.0  $\delta$  suggesting that the chelating pattern is symmetrical and has a *trans* configuration. In both the complexes of Pd(II) one broad signal at 3.5  $\delta$  is observed indicating that the ligands have an amide-NH group. It also indicates that the ligands exist in the amide form in the complexes, whereas the free ligands are in the imide form. In the Pd(II) complexes the non-involvement of the amide nitrogen in coordination (Ravinder *et al* 1984) is also confirmed by observing a broad signal at 3.5  $\delta$  as compared to the same bands in the spectra of the sodium salts of PhPMDA and PyPMDA. When the ligands exist in the amide form in the complexes the other expected peak is the carboxylic acid proton. However, no signal is present in the range 9–12 ppm indicating that the oxygen of the carboxylic group is coordinated after deprotonation. In the Pd(II) complex of PhPMDA a peak is observed at 4.2  $\delta$  and is assigned to the coordinated water molecule. The above facts have been confirmed through the deuterium exchange spectra.



In the spectrum of the Pd(II) complex, the signal of the 6'-pyridyl hydrogen atom shifts 1.3  $\delta$  downfield compared with that of PyPMDI suggesting that the pyridine N-atom is coordinated to the metal ion.

### 3.4 Electronic spectra

The reflectance spectra of  $[\text{Ni}(\text{PhPMDA})(\text{CH}_2\text{O})_2]$  is shown in figure 1. The reflectance spectra of Mn(II) complexes show three bands at 29,850, 25,250 and 18,100  $\text{cm}^{-1}$  characteristic of octahedral geometry (Thimmaiah *et al* 1985) and the electronic spectra of Fe(II) complexes show  $d-d$  bands at 11,200 and 10,800  $\text{cm}^{-1}$  characteristic of distorted octahedral geometry (Burman and Satyanarayana 1982). The three bands observed at 8,500, 15,500 and 21,000  $\text{cm}^{-1}$  in the electronic spectrum of Co(II) complexes are assigned to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  transitions, characteristic of octahedral geometry (Shah and Shah 1982). The reflectance spectra of Ni(II) complexes show three bands obtained at 10,000, 17,000 and 25,000  $\text{cm}^{-1}$ , assigned to  ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ , characteristic of octahedral geometry. The ratios of  $\nu_2/\nu_1$  in Co(II) and Ni(II) complexes are in the range 1.64 to 1.70 (Saconi 1968), which further support octahedral geometry. The Cu(II) complex of PhPMDA shows bands at 14,125 and 18,580 characteristic of square planar geometry (Fachler *et al* 1963) whereas Cu(II) PyPMDA shows a broad band at 13,000  $\text{cm}^{-1}$  and a shoulder of low intensity at 16,390  $\text{cm}^{-1}$  characteristic of tetragonal geometry (Agarwal 1981). The three bands at 15,000, 20,000 and 25,000  $\text{cm}^{-1}$  in the electronic spectra of Pd(II) complexes are assigned to  ${}^1A_{1g} \rightarrow {}^1A_{2g}$ ,  ${}^1A_{2g} \rightarrow {}^1B_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1E_g$  characteristic of square planar geometry. In addition to these, a strong charge transfer band is observed at 33,000  $\text{cm}^{-1}$  in all the Pd(II) complexes (Hazarika and Bora 1982).

### 3.5 Magnetic data

Experimental and calculated magnetic moment values are listed in table 1. The magnetic moment values observed in Mn(II), Fe(II), Co(II) and Ni(II) complexes (table 1) favour octahedral geometry. The magnetic moment value determined in Cu(II) complexes is around 1.8 B.M. indicating that the complexes are of either square planar or tetragonal geometry. In all the cases the calculated values using spin-only formula are in good agreement with the experimental values.

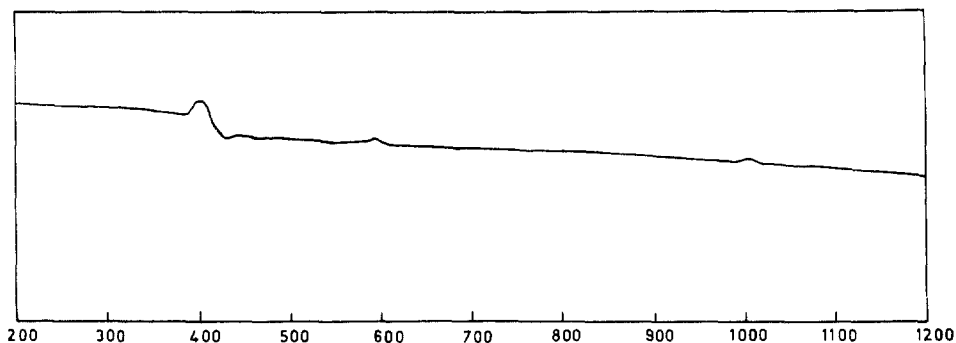


Figure 1. Reflectance spectrum of  $[\text{Ni}(\text{PhPMDA})(\text{H}_2\text{O})_2]$ .

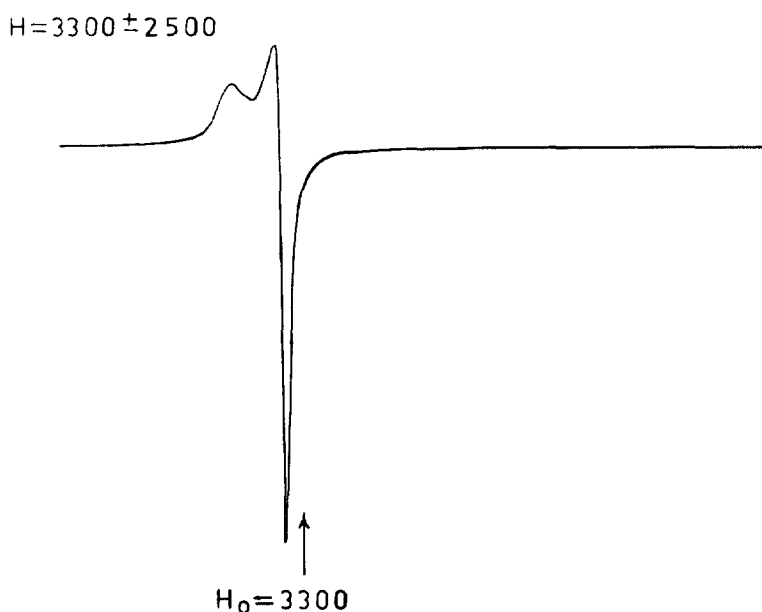


Figure 2. Electronic spin resonance of  $[\text{Cu}(\text{PhPMDA})]_n$ .

### 3.6 ESR spectra

The ESR spectra of  $[\text{Cu}(\text{PhPMDA})]_n$  recorded at room temperature in solid state are depicted in figure 2. From the two peaks, one intense absorption at high field and the other of less intensity at low field, the  $g_{\parallel}$  and  $g_{\perp}$  values have been calculated by Kneuhls method. The complexes also show anisotropic ESR spectra with  $g_{\parallel} > g_{\perp}$ , characteristic of tetragonal and square planar geometry with  $d_{x^2-y^2}$  ground state. The  $g_{\parallel}$  obtained for the Cu(II) complexes is less than 2.3 indicating covalent character of the metal ligand bond (Kovelson and Neiman 1961). The axial symmetry parameter,  $G$ , obtained for the present complexes being greater than 4 suggests no exchange interaction in solid state (Procter *et al* 1968). Further orbital reduction parameter  $k_{\parallel}$  and  $k_{\perp}$  values have been calculated which indicate the degree of delocalization of the metal electrons to the molecular orbitals of ligands. In Cu(II) complexes the extent to which  $\lambda$  is lowered from the free ion value is a measure of the extent of mixing of metal and ligand orbitals.

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