

Synthesis and Characterisation of Pd(II) and Pt(II) Complexes with Ligands Derived from 9,10-Phenanthroquinone Monoxime and Different Isomers of Diamino Benzene

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The complexes of bivalent palladium and platinum with bis-(9,10-phenanthroquinone monoximato) 1,2-diamino benzene [L_1], bis-(9,10-phenanthroquinone monoximato) 1,3-diamino benzene [L_2] and bis-(9,10-phenanthroquinone monoximato) 1,4-diamino benzene [L_3] have been synthesised and characterized on the basis of elemental analysis, magnetic susceptibility measurement, infrared and electronic spectra, conductivity measurement and ^{13}C NMR spectra.

INTRODUCTION

In view of the growing interest in monoxime complexes,¹⁻⁹ we have been investigating the coordination compounds of second and third transition series. Interest in compounds of this kind, particularly as possible bio-organic models, has led us to undertake the synthesis and characterization of a number of Schiff base metal macrocyclic compounds derived from 9,10-phenanthroquinone monoxime with *o*, *m* and *p*-diamino benzene.

We report here the synthesis and characterization of new tetradentate nitrogen donor mononuclear and binuclear macrocyclic ligands L_1 , L_2 and L_3 but our successful attempt to isolate the free ligand was possible only in case of L_1 while the remaining two ligands L_2 and L_3 were synthesized in their complex form through metal ion template synthesis.

EXPERIMENTAL

All chemicals used were of analytical grade. Phenanthroquinone and phenylene diamine were obtained from Aldrich (USA) and used without further purification.

Preparation of 9,10-phenanthroquinone monoxime

This monoxime was prepared by adding a concentrated solution of hydroxylamine hydrochloride (0.05 mol) to an alcoholic solution of 9,10-phenanthroquinone (0.05 mol) and then cooled to 5°C. To this solution we further added 20% aqueous solution of NaOH dropwise with constant stirring and the temperature of the resultant mixture was maintained below 0°C. After allowing

it to stand for about 2 h, it was diluted with water and just made acidic with glacial acetic acid. Then it was allowed to stand for 30 min followed by filtration through a suction pump. The residue was recrystallised from aqueous alcohol (60%) leaving behind a white crystalline solid having m.p. 180°C.

Bis (9,10-phenanthroquinone monoximato) 1,2-diamino benzene (L₁)

1,2-Diaminobenzene (0.01 mol) was titrated with 9,10-phenanthroquinone monoxime (0.02 mol) with the help of agate and mortar for nearly 2 h. The reaction mixture was kept in a refrigerator overnight. The compound was dried under vacuum and recrystallised from a minimum use of alcohol as solvent. The m.p. was found to be 205°C.

Bis-(9,10-phenanthroquinone monoximato) 1,2-diamino benzene metal(II) [M(L₁)]₂; M = Pd(II) or Pt(II)

The metal complexes were synthesised by refluxing a mixture of aqueous solution of K₂PdCl₄/K₂PtCl₄ and ligand solution in tetrahydrofuran (1 : 1) on a water bath for 6 h. The complexes were isolated by breaking the resulting solution over crushed ice. The product was filtered, washed and dried in an oven. It was then recrystallised with ethanol and further washed and dried.

Di-[bis-(9,10-phenanthroquinone monoximato, 1,3-diamino benzene) di metal(II) [M(L₂)]₂; M = Pd(II) or Pt(II)

To an aqueous solution of metal(II) chloride (0.005 mol), an alcoholic solution of 9,10-phenanthroquinone monoxime (0.01 mol) was added with constant shaking. Then an alcoholic solution of 1,3-diamino benzene (0.005 mol) was added to this solution slowly with constant shaking. It was refluxed on a water bath for 7 h. On cooling at room temperature greenish and yellowish coloured residues were left behind which were subsequently washed with alcohol and finally with ether and recrystallised with absolute alcohol.

Same process was adopted for the preparation of complexes with 1,4-diamino benzene, *i.e.*, [ML₃].

The crystallised complexes were analysed for their constitutional elements to find out the molecular formula. IR spectra (KBr) were recorded on a Perkin-Elmer FT 1600 spectrophotometer and electronic spectra on a Unicam UV-2-300 spectrophotometer. Magnetic moment was determined using Gouy's method where as molar conductivities were determined by using OK-102 Radelkis conductivity meter. The magnetic susceptibility measurement was made on a Faraday balance at room temperature. ¹³C NMR spectra (CDCl₃) were recorded on a Varian Gemini 300 BB instrument.

RESULTS AND DISCUSSION

The physico-chemical parameters of metal complexes are presented in Table-1. The important vibrational bands of the ligand and the metal complexes are given in Table-2. The IR spectrum of the ligand H₂L showing a band in the region

3250 cm^{-1} is due to —OH stretching vibrations of oxime groups^{10, 11} which is absent in these complexes. A band that appeared in the vicinity of 1650 cm^{-1} is due to $\nu(\text{C}=\text{N})$ of oxime group both in the ligand and complexes. This band in the complex has been shifted to lower frequency region whereas $\nu(\text{N}=\text{O})$ is slightly perturbed but $\delta(\text{O}=\text{H})$ is absent showing that $>\text{C}=\text{N}-\text{O}$ group is present and bonding occurs through N atom to the metal M(II) ion^{12, 13}.

TABLE-1
PHYSICO-CHEMICAL PARAMETERS OF M(II) COMPLEXES OF LIGANDS
 L_1, L_2 AND L_3 , M = Pd(II) AND Pt(II)

Complex (colour)	m.w.	Molar conductivity in $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$.	% Analysis, found (calcd.)			
			C	H	N	M
[Pd(L_1)] (Yellowish)	590.40	15.8	68.90 (69.10)	3.15 (3.38)	9.25 (9.48)	17.86 (18.02)
[Pd(L_2) ₂] ₂ (Military green)	1080.80	18.6	68.80 (69.10)	3.10 (3.38)	9.15 (9.48)	17.78 (18.02)
[Pd(L_3) ₃] ₃ (Dark green)	1080.80	18.7	68.35 (69.10)	2.95 (3.38)	8.95 (9.48)	17.65 (18.02)
[Pt(L_1)] (Greenish yellow)	679.09	16.3	59.85 (60.08)	2.65 (2.94)	8.10 (8.24)	28.45 (28.72)
[Pt(L_2) ₂] ₂ (Yellow)	1358.18	20.4	59.75 (60.08)	2.55 (2.94)	7.85 (8.24)	27.85 (28.72)
[Pt(L_3) ₂] ₃ (Yellow)	1358.18	20.6	59.95 (60.08)	2.75 (2.94)	8.10 (8.24)	28.35 (28.72)

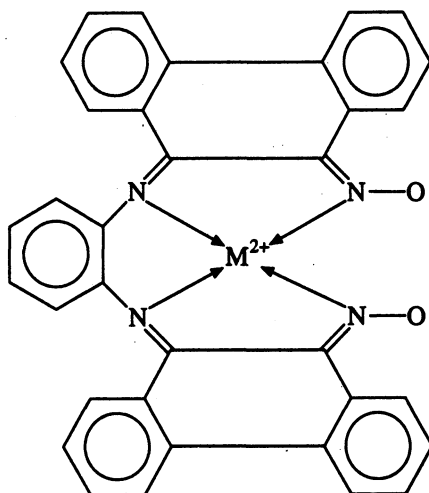
L_1 = Bis-(9,10-phenanthroquinone monoximato) 1,2-diamino benzene.

L_2 = Bis-(9,10-phenanthroquinone monoximato) 1,3-diamino benzene.

L_3 = Bis-(9,10-phenanthroquinone monoximato) 1,4-diamino benzene.

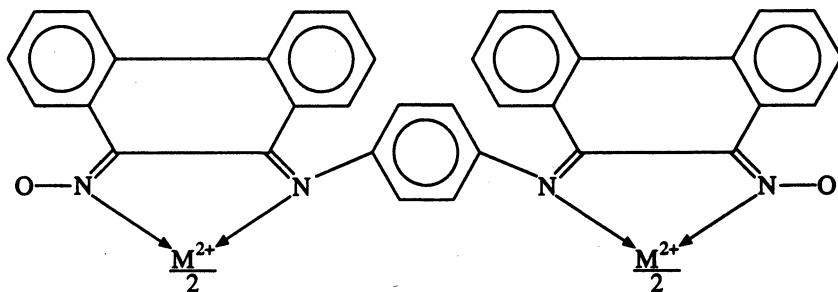
TABLE-2
KEY INFRARED SPECTRAL DATA (cm^{-1}) OF LIGAND AND COMPLEXES IN cm^{-1}

Ligand Complexes	IR spectral data				UV-visible spectral data		
	$\nu(\text{O}=\text{H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{O})$	$\nu(\text{M}=\text{N})$	${}^1A_{1g} \rightarrow {}^1A_{2g}$	${}^1A_{1g} \rightarrow {}^1B_{1g}$	${}^1A_{1g} \rightarrow {}^1E_{1g}$
L_1	3250	1650	1170	—			
[Pd(L_1)]	—	1610	1160	495	17,500	22,100	31,500
[Pd(L_2) ₂] ₂	—	1595	1165	490	17,800	22,250	31,300
[Pd(L_3) ₃] ₃	—	1590	1165	495	17,700	22,300	31,200
[Pt(L_1)]	—	1615	1180	500	21,800	26,200	30,800
[Pt(L_2) ₂] ₂	—	1590	1165	510	21,900	26,300	30,500
[Pt(L_3) ₂] ₃	—	1595	1155	520	21,600	26,400	30,600



M = Pd(II), Pt(II)

Fig. 1



M = Pd(II), Pt(II)

Fig. 2

In far infrared region prominent bands which are slightly observed in the spectra of metal(II) complexes, it is very difficult to identify metal-ligand vibrations in the complexes. However, the bands observed in the vicinity of 500 cm^{-1} region are assignable to $\nu(\text{M}-\text{N})$ band¹⁴⁻¹⁶.

The Pd(II) complexes are diamagnetic. The electronic spectral bands near $17,500$, $22,100$ and $31,500\text{ cm}^{-1}$ may be assigned to ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$, ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_{1g}$ transitions respectively in a square planar configuration around Pd(II). The Pt(II) complexes are also diamagnetic. The electronic spectrum displays three bands near $21,800$, $26,200$ and $30,500\text{ cm}^{-1}$ which may be assigned to ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$, ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_{1g}$ transitions respectively in a square planar symmetry^{17, 18}.

Literature presents both ^1H and ^{13}C NMR spectra¹⁹ in the detection of coordination activity, but the former is rarely successful owing to the difficulty of evaluating the contribution of group anisotropy effect. The application of ^{13}C NMR spectra in the detection of coordination activity is more encouraging with the carbon atoms of the $>\text{C}=\text{N}$ groups if moved high field when the N atom is coordinated. Taking into account the finding ^{13}C NMR spectra of $>\text{C}=\text{N}$ and the complexes with Pd(II) and Pt(II) were analysed. But in our case, the signals due to carbon atom of the $>\text{C}=\text{N}$ group in the coordinated ligands were observed at lower field ($\delta \text{C}=\text{N}$ 166.2, 150.3 and 158.4 ppm) than those of free ligand ($\delta \text{C}=\text{N}$ 154.2, 135.7 and 145.5 ppm).

The complexes are coloured yellow and greenish, air stable, with generally low solubility in organic solvents. Molar conductivity in nitromethane (10^{-3} M) shows the complexes to be non-conducting (λ_m range 15.8–20.6 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$).

On the basis of spectral and analytical data, it seems reasonable to assume that complexes of Pd(II) and Pt(II) have square-planar structure as shown in Figs. 1 and 2.

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