

Transition Metal Complexes of Phenhomazine Derivative (DIBENZO[b,f][1,5]Diazocine-6:12-Dione with Copper(II), Cadmium(II), Mercury(II) and Zinc(II))

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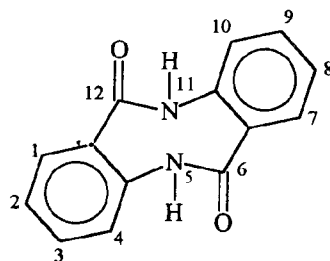
Summary: The eight membered cyclic diamine are versatile chelating agents and often exhibit the ability to confer various geometries on their complexes. The complexes of dibenzo[b,f][1:5]diazocine-6:12-dione (commonly called dianthranilide) are reported with that of salts of copper, zinc, cadmium and mercury. The titled compound can be viewed as modified form of DACO and PHZ, in which the vibrational freedom of carbon (C₆ and C₁₂) is further restricted by fusing with oxygen. The structure of the complexes is assigned on the analysis of their spectral, magnetic and conductance data. The molecular weight of the ligand is confirmed by its electron impact mass spectrum.

Introduction

Medium ring diamine ligands are versatile chelating agents and often exhibit the ability to stabilize various geometries and provide a link between acyclic and mesocyclic chelating agents. The molecular properties of these complexes are controlled by their unique steric requirements e.g. 1,5-diazacyclooctane (daco) a eight member cyclic-diamine forms stable four coordinated planar complexes with copper(II) and nickel(II) and five coordinated complexes with cobalt(II), where as seven member cyclicdiamine, 1,4-diazacycloheptane (dach) [1-8] forms only five coordinated complexes

with these metal ions. The modified form of these ligands such as 5, 6,11,12-tetrahydro-2:8-dimethyl-phenhomazine (PHZ), 5,6,11,12-tetrahydro-2:5:8-trimethylphenhomazine (MPHZ) and 5,6,11,12-tetrahydro-2:8-dimethyl-15:11-endomethylenephenhomazine(EPHZ) can be viewed as eight membered cyclicdiamine in which vibrational freedom of two methylene carbons restricted being fused with benzene rings and thus making more room for 5th and 6th coordination. In spite of this PHZ, EPHZ and MPHZ form four coordinated complexes of square planar and tetrahedral geometry [9,10].

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Dibenzo[b,f][1:5]diazocin-6:12-dione
(PHZD)

Dibenzo[b,f][1,5]diazocine-6:12-dione [PHZD] which is further modified form of PHZ in which C₆ and C₁₂ are being fused with oxygen and thus making it more powerful chelating agent due to the available unshared electrons on oxygen. It forms mono complexes with copper(II), cobalt(II), nickel(II) and zinc(II) with sulphate as anion. The complexes of these metal ions are square planar in geometry except that of zinc(II) which is tetrahedral [11].

The present study, reports the complexes of PHZD of copper(II), zinc(II), cadmium(II) and mercury(II) with Cl⁻, Br⁻, I⁻ and NO₃⁻ as anions. The molecular structures are explained on the basis of analytical, spectroscopic, magnetic and conductance data. The thermal analyses are underway and is subject of future communication.

Results and Discussion

The ligand is confirmed by its melting point, NMR and mass spectrum. The analytical data of PHZD complexes are in consistent with the formula [Cu(PHZD)₂X₂], [Zn(PHZD)₂X₂] [Cd(PHZD)₂X₂] and [Hg(PHZD)₂X₂] for copper(II), zinc(II), cadmium(II) and mercury(II) respectively where X = Cl⁻, Br⁻, I⁻ and NO₃⁻. The bis nature of these complexes is in resemblance with that of PHZ and EPHZ. The conductance data show the non-electrolytic behaviour of these complexes.

Copper complexes

The elemental analysis of copper-PHZD complexes suggest the [Cu(PHZD)₂X₂] molecular formula. The electronic spectra of mono and bis-PHZD complexes of copper(II) have been explained earlier [8-10]. The conductance and spectral data support

tetragonally distorted octahedral complexes when anions are nitrate or halides. In case of sulphate complex of PHZD penta coordinated complexes are observed [11]. The electronic absorption spectra of bis complexes exhibit a single absorption peak in the region 600-710 nm (Fig. 1). The blue or green colour of the complexes are due to the presence of absorption band in the region 640-750 nm [12,13]. The envelope of these bands are generally unsymmetrical seeming to encompass several overlapping transitions. The magnetic moment of copper(II) complexes is near to 1.8 B.M, which is very close to the spin only value for the unpaired electron.

The infrared spectra shows the coordination of PHZD through the nitrogen and no evidence of involvement of oxygen of carbonyl is observed as this frequency remains unshifted. In the far ir region the M-N band is observed. The non-electrolytic behaviour further support the assigned geometry.

Complexes of Cadmium(II), Mercury(II) and Zinc(II)

In view of the well known tendencies of Cd(II), Hg(II) and Zn(II) to form tetrahedral geometries, it may be reasonably proposed tetrahedral geometry with PHZD acting as monodentate ligand. It is worth mentioning here that PHZD like MPHZ formed mono complexes with ZnSO₄, whereas metal halides yielded bis-complexes. The assigned tetrahedral geometry of these complexes further supported by conductance data.

Experimental

Materials

Metal salts of copper(II), cadmium(II), mercury(II) and zinc(II) were obtained from standard source suppliers. They were of analytical grade and were used without further purification. The nonaqueous solvents used in synthetic work were distilled twice and were properly dried.

Ligand

Anthraquinone dioxime (2 gm) was stirred into polyphosphoric acid (50 gm) at 100°C and the mixture was, thereafter, constantly heated in an oil bath at 140°C for 80 minutes. The dissolution

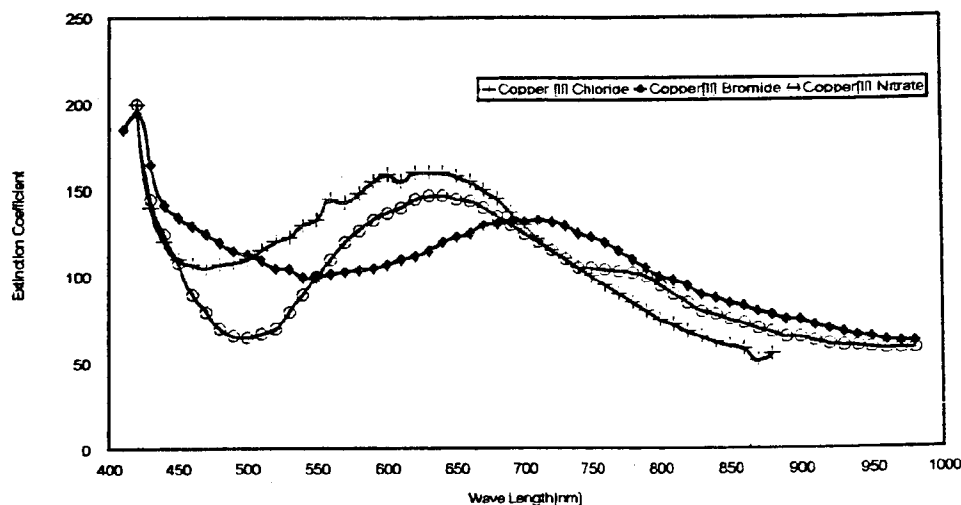


Fig. 1: Absorption spectra of copper(II) PHZD complexes in Nitromethane.

completed in 60 minutes. The product was poured into 300 ml of cold water. The precipitated solid was filtered under vacuum and recrystallized from water having melting point 334°C (lit. m.p. 334°C), Yield 1.7 gm, 85% [14].

Preparation of complexes

The complexes of salts mentioned above were prepared in a three-necked flask using non-aqueous solvent by the following general procedure:

A required amount of partially dehydrated salt was dissolved in a minimum amount of methanol/ethanol mixture. For the preparation of all complexes 1:2 metal/ligand ratio was employed. The ligand (in methanol/ethanol mixture) was slowly added to the metal ion solution and was stirred for 3-4 hours. The complexes were precipitated either on standing or on evaporation in vacuum at 50°C. The product obtained were filtered through sintered glass crucible, washed several times with dry acetone.

Table-1: Elemental Analysis of PHZD and its complexes*

Compound	M.wt.	Colour	M.P. °C	C%	N%	H%	Cation %	Anion %
$C_{14}H_{10}N_2O_2$	238	White	334	70.45 (70.60)	11.70 (11.75)	4.50 (4.20)	--	--
$Cu(C_{14}H_{10}N_2O_2)_2Cl_2$	610.5	Sea green	310	55.42 (55.03)	9.20 (9.17)	3.38 (3.27)	10.21 (11.41)	11.13 (11.63)
$Cu(C_{14}H_{10}N_2O_2)_2Br_2$	699.3	Green	315	48.24 (48.03)	8.21 (8.01)	3.01 (2.86)	8.87 (9.09)	23.20 (22.88)
$Cu(C_{14}H_{10}N_2O_2)_2(NO_3)_2$	663.5	Green	270	50.46 (50.63)	12.33 (12.66)	3.21 (3.01)	9.88 (9.58)	--
$Cd(C_{14}H_{10}N_2O_2)_2Cl_2$	659.4	White	310	53.99 (50.96)	9.42 (8.49)	4.13 (3.93)	16.81 (17.05)	11.12 (10.77)
$Cd(C_{14}H_{10}N_2O_2)_2Br_2$	748.2	White	285	44.63 (44.90)	7.31 (7.46)	2.54 (2.67)	15.58 (15.02)	21.65 (21.38)
$Cd(C_{14}H_{10}N_2O_2)_2(NO_3)_2$	712.4	White	300	47.59 (47.16)	11.27 (11.79)	3.06 (2.81)	15.23 (15.78)	--
$Zn(C_{14}H_{10}N_2O_2)_2Cl_2$	612.3	White	290	54.61 (54.87)	9.30 (9.14)	3.18 (3.27)	11.22 (10.68)	11.96 (11.59)
$Zn(C_{14}H_{10}N_2O_2)_2(NO_3)_2$	665.3	White	250	50.25 (50.50)	12.54 (12.62)	2.89 (3.00)	9.36 (9.83)	--
$Hg(C_{14}H_{10}N_2O_2)_2Cl_2$	747.5	Off white	190	44.69 (44.95)	7.24 (7.49)	2.73 (2.68)	26.98 (26.83)	8.99 (9.50)
$Hg(C_{14}H_{10}N_2O_2)_2I_2$	930.3	Off white	200	35.98 (36.98)	6.28 (6.02)	2.03 (2.15)	21.27 (21.56)	26.87 (27.28)

*Theoretical percentages are given in parenthesis

Table-2: Magnetic and conductance data for PHZD complexes

Compound	Temp K°	Λ (mho mol ⁻¹ cm ³)	$10^6 \cdot X_M^{corr}$ (egsu)	μ_{eff} (B.M)*
[Cu(PHZD) ₂ Cl ₂]	298	19 Non-elec	1355	1.81
[Cu(PHZD) ₂ Br ₂]	298	22 Non-elec	1253	1.75
[Cu(PHZD) ₂ (NO ₃) ₂]	298	45 Non-elec	1311	1.79
[Cd(PHZD) ₂ Cl ₂]	303	19 Non-elec	--	Diamagnetic
[Cd(PHZD) ₂ Br ₂]	298	17 Non-elec	--	Diamagnetic
[Cd(PHZD) ₂ (NO ₃) ₂]	298	21 Non-elec	--	Diamagnetic
[Zn(PHZD) ₂ Cl ₂]	298	16 Non-elec	--	Diamagnetic
[Zn(PHZD) ₂ (NO ₃) ₂]	298	23 Non-elec	--	Diamagnetic
[Hg(PHZD) ₂ Cl ₂]	298	09 Non-elec	--	Diamagnetic
[Hg(PHZD) ₂ Br ₂]	298	07 Non-elec	--	Diamagnetic

* $\mu_{eff} = 2.84 \sqrt{X_M} = T$

susceptibilities of crystalline complexes for the diamagnetism of the ligand and the anions involved [16].

Electrolytic conductance measurements (Table-2)

The electrolytic conductance of the complexes were determined by conductivity bridge made by Mullard, Inc England. The conductivity cell was properly calibrated. The observed conductivity was always corrected for the specific conductance of the pure solvent used [17].

Table-3: IR bands of PHZD and its complexes*

Compound	ν_{N-H}	$\nu_{C=O}$	Aromatic ring	Significant bands	M-N
PHZD	3200vs	1640s	1600s, 1570s, 1500s, 1450s	1100s, 760s, 750s, 600s, 400s	--
[Cu(PHZD) ₂ Cl ₂]	3110s	1640s	1600s, 1570w, 1500s, 1450s	1100s, 760w, 750w, 600s, 400s	310w
[Cu(PHZD) ₂ Br ₂]	3100s	1640s	1600s, 1570w, 1500s, 1450s	1100s, 760w, 750w, 600s, 400s	310w
[Cu(PHZD) ₂ (NO ₃) ₂]	3100b	1640s	1600s, 1570w, 1500s, 1450s	1100s, 760w, 750w, 600s, 400s	310w
[Cd(PHZD) ₂ Cl ₂]	3200b 3110b	1640s	1600s, 1570w, 1450w	1100s, 760w, 400s	--
[Cd(PHZD) ₂ Br ₂]	3000b 3100b	1640s	1600b, 1570w, 1500w	1100s, 760w, 750w, 600s	--
[Cd(PHZD) ₂ (NO ₃) ₂]	3200s 2950b	1640s	1600s, 1570w, 1500s, 1450s	1100s, 760w, 750w, 400s	310w
[Zn(PHZD) ₂ Cl ₂]	3200b 3110b	1640s	1600s, 1570w, 1450s	1100, 760w, 400s	--
[Zn(PHZD) ₂ (NO ₃) ₂]	3200s 2950b	1640s	1600s, 1570w, 1500s, 1450s	1100s, 760w, 750w, 400s, 600s	310w
[Hg(PHZD) ₂ Cl ₂]	3200m 3100b	1640s	1600s, 1570w, 1500w	1100s, 760w, 750w, 600s	
[Hg(PHZD) ₂ Br ₂]	3200m 3100b	1640s	1600s, 1570w, 1500w	1100s, 760w, 750w, 600s	

*s: sharp; vs: very sharp; b: broad; m: medium; w: weak

dried under vacuum and recrystallized from suitable solvents.

Analytical data (Table-1)

Cations were determined by using XRF-500 link system England, and C, H, and N elemental analysis were performed through the courtesy of H.E.J. Research Institute of Chemistry, University of Karachi on Carloerba Mod 1106, whereas anion was determined by usual method [15].

Magnetic susceptibility measurements (Table-2)

The magnetic moments of the solid complexes at room temperature were determined by the Gouy method. A double ended Gouy tube was calibrated using Hg[Co(SCN)₄] as standard. Pascal's constants were used to determine molar

Infra-red spectra (Table-3)

The Infra-red absorption spectra (KBr disc) of the solid complexes were obtained with I.R. Spectrophotometer Model SP-3-100 PYE Unicam A.M.

UV-visible spectra (Table-4)

Visible and ultraviolet spectra of the complexes in different solvents were obtained with Jasco Unidec-1 recording spectrophotometer using set matched 1 cm quartz cells. The absorption spectra were always recorded using freshly prepared solutions.

Table-4: UV, visible spectra of PHZD complexes

Complex	λ [nm]	ϵ_{max} [M ⁻¹ cm ⁻¹]	Comments
[Cu(PHZD) ₂ Cl ₂]	630	160	² E _g → ² T _{2g}
[Cu(PHZD) ₂ Br ₂]	710	133	² E _g → ² T _{2g}
[Cu(PHZD) ₂ (NO ₃) ₂]	640	140	² E _g → ² T _{2g}

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