Inorganica Chimica Acta, 60 (1982) 231–238

Synthesis and Structural Studies of Transition Metal Complexes of Cyclic Amidines*

M. SAKHAWAT HUSSAIN and SAEED-UR-REHMAN

Department of Chemistry, University of Petroleum and Minerals, Dhahran Airport Box 144, Dhahran, Saudi Arabia

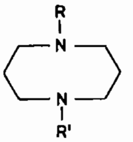
Received September 18, 1981

Cyclic amidines PHZ and MPHZ (shown below) can be viewed as eight-membered cyclic diamines with two of the methylene carbons fused to the benzene rings. Although the axial positions in the bis-complexes of PHZ and MPHZ are open for fifth and sixth coordination, only four-coordinated complexes with copper(II), cobalt(II), nickel(II) and zinc(II) could be prepared. The molecular structures of these compounds and of some palladium(II), platinum(II) and platinum(IV) compounds are explained on the basis of their analytical, spectroscopic, magnetic and conductance data. Thermogravimetric analyses were carried out to explain mode of decomposition. The results show that complexation of cyclic amidines is not only sterically controlled, but factors such as unusual chelate bite angle, multiple chelate ring formation and crystal field stabilization play important role in affecting the stability and coordination number of the complexes.

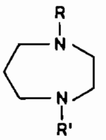
Introduction

Medium ring systems (Mesocycles) provide a link between acyclic and macrocyclic chelating agents. The molecular properties of the complexes formed by mesocycles are often controlled by their unique steric requirements and are different from the complexes of acyclic ligands. For example, 1,5-diazacyclooctane (daco, I) forms stable four-coordinated planar complexes with copper(II) and nickel(II) [1] and five-coordinated cobalt(II) complexes [2]. Seven-membered cyclic diamine, 1,4-diazacycloheptane (dach, V) forms only five-coordinated complexes [3, 4]. Similar complexes of mesocyclic dithioethers, 1,5-dithiocyclooctane (dtco, IV) and 1,4-dithiocycloheptane (dtch, VIII) were reported with nickel(II) and copper(II) [5]. Modification of the cyclic diamines with acetate and ethylamine functions produces tridentate, daco-monoacetate(II) and N-(2-aminoethyl)1,4-diazacycloheptane(VI), and tetradentate, daco-diacetate(III) and N,N′-bis(2-aminoethyl)1,4-diazacycloheptane(VII) [6, 7]. The ability to confer various geometries by these mesocycles on the central metal ions and the stabilities of their complexes are explained primarily on the basis of effective shielding of the axial positions, since in all known cases chelation of a mesocycle causes blockage of at least one such position forbidding the formation of six-coordinated species.

I-IV V-VIII

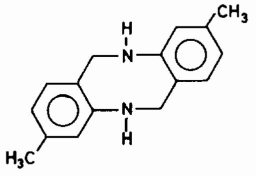


I - IV V - VIII

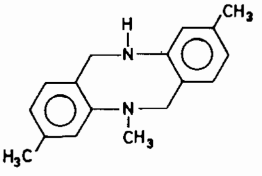


I daco : $R = R' = H$
II daco-mac : $R = CH_3COO^-$
III daco-diac : $R = R = CH_3COO^-$
IV dtco : $N = S$ none R
V dach : $R = R' = H$
VI dach-men : $R = CH_2CH_2NH_2$ $R = H$
VII dach-dien : $R = R = CH_2CH_2NH_2$
VIII dtch: $N = S$ none R

The title cyclic amidines (IX & X) can be viewed as modified eight-membered cyclic diamines with vibrational freedom of the two methylene carbons restricted by their being a part of the benzene rings. Molecular models indicate that the axial positions in the bis-complexes of these amidines are open for fifth and/or sixth coordination. Therefore, these amidines should form six-coordinated species if blocking of the axial position is the only factor forcing exclusive formation of four- and five-coordinated complexes.



(IX, PHZ)



(X, MPHZ)

---

*Presented at the American Chemical Society 17th Midwest Regional Meeting held at the University of Missouri, Columbia, U.S.A., on November 5–6, 1981. (Abstract No. 415).

0020-1693/82/0000-0000/$02.75

The present study reports the synthesis of a few new complexes of PHZ with copper(II), nickel(II), palladium(II) and platinum(IV). The synthesis and spectroscopic data of some complexes of PHZ with copper(II), nickel(II) and zinc(II) were reported earlier [8]. The complexes of MPHZ with cobalt(II), nickel(II), copper(II), zinc(II), palladium(II) and platinum(IV) are also included in the present work. The molecular structures are explained on the basis of the analytical, spectroscopic, magnetic and conductance data. The X-ray crystal structure of $[Ni(PHZ)_2](ClO_4)_2$ has been determined and is the subject of a future communication.

Experimental

Reagents

Metal halides and sulfates were obtained from E. Merck and were used without further purification. The perchlorates of Nickel(II) and Copper(II) were prepared by treating the corresponding carbonates with perchloric acid in 1:2 molar ratio. The perchlorates formed were recrystallized at least three times from perchloric acid. All complexes were prepared using non-aqueous solvents which were properly dried and distilled at least twice before using.

Ligands

The ligand 5:6:11:12-Tetrahydro-2:8-dimethylphenhomazine (PHZ) was prepared by the procedure of Cooper and Partridge [9]. The methylated ligand, 5:6:11 - Trihydro - 2:8:12 - trimethylphenhomazine (MPHZ), was obtained by the reaction of PHZ with dimethylsulfate using the method of Wagner [10]. PHZ was recrystallized twice from benzene whereas MPHZ was recrystallized from petroleum ether.

Preparation of the Complexes and Analytical Data

The metal salts were dehydrated by shaking with a slight excess over the calculated amount of 2,3-dimethoxypropane, for 2 to 4 hours. The complexes were prepared by slow addition of an excess of the ligand solution to the metal solution with constant stirring. In the case of PHZ complexes hot anhydrous butanol was used as a solvent, whereas anhydrous methanol was used for the preparation of MPHZ complexes. The complexes were precipitated at once in most cases; sometimes the solid product was obtained by removing a part of solvent under vacuum. The products were filtered through sintered glass crucible, washed several times with butanol or methanol and dried under vacuum at room temperature. The yield ranged from 40 to 60%. Because of the possible danger of explosion, the perchlorates were dried by leaving in a vacuum desiccator over a period of several days.

Spectroscopic Measurements

The infrared absorption spectra of the solid complexes were obtained with JASCO IR-1 and Perkin Elmer Model 577 spectrophotometers, while Far I.R. spectra were obtained with a Beckman I.R. 2440 spectrophotometer. The I.R. spectra were usually examined in nujol mull supported on NaCl, KBr or CsI plates. In some cases, the spectra were measured using KBr pellets.

The visible and ultraviolet spectra of the complexes in different solvents were obtained with a JASCO UNIDAC-1 recording spectrophotometer with a set of matched 1-cm quartz cells. The spectra were always recorded using freshly prepared solutions, though the complexes were fairly stable in nitromethane and dimethylsulphoxide. The solid state spectra were measured by placing a filter paper (Whatman No. 1) soaked in the Nujol mull of the complex into the beam of the spectrophotometer in place of the cell [11].

The proton-NMR data were obtained in $DMSO-d_6$ using Varian Associates EM-360 and JNM-PMX 60 spectrometers. Tetramethylsilane (TMS) was used as an external standard.

Thermogravimetric Analysis

Thermogravimetric analyses of the analytically pure anhydrous complexes were carried out in air using a Recording Stanton (England) thermogravimetric balance. Triplicate measurements were made for each complex. The occurrence of a horizontal portion in the curve is taken as evidence that the substance remains constant in weight throughout the temperature range corresponding to that horizontal. The rate of heating was 5 ℃ per min, and the compounds were heated up to 650 ℃. No thermogravimetric studies were done on perchlorato complexes because of the explosive nature of perchlorate.

Electrolytic Conductance and Magnetic Susceptibility Measurements

A conductivity bridge (Mullard Equipment Limited, London) and a conductivity meter (Type OK 102/I Radelkiss, Electro-chemical Instruments, Hungary) were used to measure conductivities of the complexes in various solvents. The conductivities of the pure salts were also measured in the same solvent for the purpose of comparison of the conductivities of the pure metal salts with those of the complexes. The cell constants were calculated using 0.1 molar solutions of potassium chloride [12] prepared in conductivity water. The observed conductivities were corrected for the specific conductance of pure solvents determined under similar conditions.

The magnetic moments of the solid complexes were determined by the Gouy method at room temperature. A double-ended Gouy tube was calibrated using $Hg[Co(SCN)_4]$ as the standard [13]. The magnetic susceptibility of this compound was taken as 16.44×10^{-6} c.g.s. units at 20 ℃. The observed molar susceptibilities of the complexes were corrected for the diamagnetism of the ligands and the magnetic moments were calculated according to the procedure described by Figgs and Lewis [13].

Results

The elemental analysis of the PHZ and MPHZ complexes was done at the Micro Analytical Laboratory, Carlton Road, Oxford, England. Metal ions and anions were determined using usual volumetric and spectrophotometric procedures. The results are reported in Table I and II. All complexes are soluble in nitromethane, insoluble in water, benzene and slightly soluble in acetone, methanol and butanol.

Analytical data (Table I) of PHZ complexes are consistent with the formula $[M(PHZ)_2]X_2$ when M = Ni(II), Cu(II), Zn(II), Pd(II), Pt(II and IV) and X = Cl^-, Br^-, I^-, NO_3^-, $So_4^=$ and ClO_4^-. Only mono-complexes of Co(II), Ni(II), Cu(II), Zn(II), Pt(II) and Pt(IV) were formed with MPHZ (Table II). In contrast to the behavior of PHZ which resembles that of daco, the MPHZ did not form any bis-complexes with first-row metals even when a very large excess of the ligand was used. Although N-methylation of PHZ might be expected to cause increased complex stability due to an increased basicity, steric factors seem to dominate the complexation reactions of MPHZ.

The visible and ultraviolet spectra of $[Ni(MPHZ)_2Cl_2]$ and $[Cu(PHZ)_2SO_4]$ in nitromethane are shown in Fig. 2 and of Copper(II) and Cobalt(II) complexes of MPHZ are given in Fig. 3 and 4. The proton-NMR data for the ligands and some of the diamagnetic complexes are reported in Table III. The results of thermogravimetric analyses are tabulated in Table IV, the values for molar conductance in nitromethane and of magnetic measurements are given in Table V,

Discussion

Spectroscopic, Magnetic and Conductance Studies

The ^{1}H-nmr spectra of ligands and of some diamagnetic complexes in DMSO-d_6 clearly exhibit four peaks for PHZ and its complexes and five peaks for MPHZ and its complexes. The ratio of the integrated intensities of various peaks agrees well with the calculated ratio of the number of protons of various kinds. In all complexes essentially the same chemical shift values were observed as for the free ligands, except for N–H and N–CH_3 proton resonances which shifted slightly to lower values suggesting coordination through the amine nitrogens.

The infrared spectra for the free PHZ have a sharp band at 3350 cm^{-1} for the N–H stretching frequency, whereas in MPHZ the N–H band was observed at 3390 cm^{-1} and the N–CH_3 band was observed at 1180 cm^{-1}. Another strong band at 1610 cm^{-1} was observed in both ligands. All these bands are shifted significantly to lower frequencies in complexes and

TABLE I. Analytical Data of 5:6:11:12-Tetrahydro-2:8-dimethylphenhomazine (PHZ) Complexes*

Complex	Color	Dec. Pt. ℃	C %	H %	N %	Metal %	Anion %
PHZ	White	204	80.78 (80.70)	11.69 (11.73)	7.64 (7.58)	–	–
$Cu(PHZ)_2(ClO_4)_2$	Green	170	52.06 (51.90)	4.92 (4.87)	7.66 (7.58)	9.20 (8.53)	–
$Cu(PHZ)_2SO_4$	Green	255	61.25 (60.47)	5.86 (5.67)	8.32 (8.82)	9.25 (9.92)	–
$Ni(PHZ)_2(ClO_4)_2$	Yellow	254	53.14 (52.24)	5.12 (5.45)	8.81 (9.15)	9.50 (8.46)	–
$Ni(PHZ)_2SO_4$	Yellow	201	60.62 (60.85)	5.54 (5.71)	8.10 (7.96)	10.50 (9.55)	15.60 (15.70)
$Pd(PHZ)_2Cl_2 \cdot 2HCl$	Yellow	221	49.92 (49.92)	5.12 (4.90)	7.60 (7.30)	– –	– –
$Pt(PHZ)Cl_2 \cdot 2HCl$	Brown	190	34.28 (33.27)	3.65 (3.42)	5.08 (4.85)	– –	25.46 (24.61)
$Pt(PHZ)_2Cl_4 \cdot 2HCl$	Yellow	196	43.67 (43.34)	4.42 (4.06)	6.12 (6.32)	–	–

*Calculated percentages are given in parentheses. The analyses of the metal ions and anions were performed using usual analytical procedures.

TABLE II. Analytical Data of 5:6:11-Trihydro-2:8:12-trimethylphenhomazine (MPHZ) Complexes*.

Complex	Color	Dec. Pt. °C	C %	H %	N %	Metal %	Anion %
Co(MPHZ)Cl_2	Green	89	52.91 (53.40)	5.25 (5.23)	7.46 (7.33)	16.20 (15.40)	17.50 (18.50)
Co(MPHZ)Br_2	Green	96	43.62 (43.33)	4.28 (4.25)	5.98 (5.94)	13.46 (12.52)	34.70 (33.97)
Ni(MPHZ)Cl_2	Green	106	53.31 (53.40)	5.06 (5.23)	7.31 (7.33)	15.90 (15.40)	19.60 (18.30)
Cu(MPHZ)Cl_2	Green	131	53.01 (52.80)	5.10 (5.18)	7.39 (7.25)	15.40 (16.32)	17.50 (18.39)
Cu(MPHZ)Br_2	Green	93	41.36 (42.96)	3.97 (4.20)	4.72 (5.89)	12.52 (13.26)	32.00 (33.69)
Cu(MPHZ)SO_4	Green	150	51.70 (49.63)	5.20 (4.86)	7.25 (6.81)	15.30 (15.32)	23.75 (23.35)
Zn(MPHZ)Br_2	White	284	42.12 (42.77)	4.35 (4.19)	6.02 (5.87)	12.80 (13.63)	32.00 (33.50)
Pd(MPHZ)Cl_2·2HCl	Light brown	179	40.43 (40.69)	4.56 (4.38)	5.81 (5.57)	– –	– –
Pt$(MPHZ)_2Cl_2$	Grey	140	53.57 (52.92)	5.69 (5.19)	7.61 (7.26)	–	–
Pt(MPHZ)$Cl_4$2HCl	Light yellow	132	30.28 (30.80)	3.26 (3.32)	4.15 (4.22)	–	–

*Calculated percentages are given in parentheses.

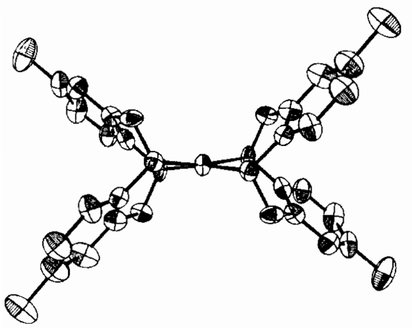


Fig. 1. ORTEP projection of $[Ni(PHZ)_2]^{2+}$ showing the boat configuration of eight-membered ring of PHZ with a minimum non-bonded interaction leaving the axial positions on the metal unshielded.

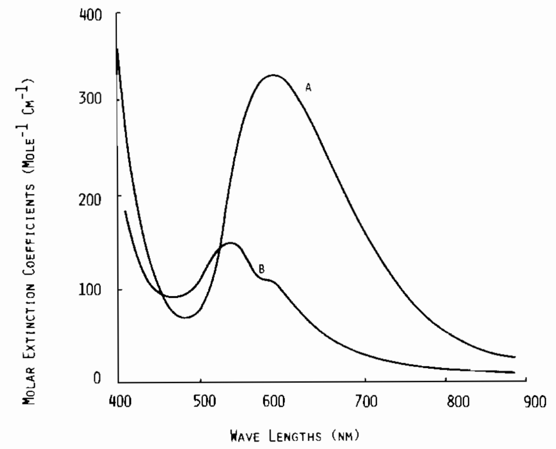


Fig. 2. Visible absorption spectra of (A) [Ni(MPHZ)Cl_2] and (B) $[Cu(PHZ)_2SO_4]$ in nitromethane.

become broad, sometimes split up, suggesting coordination through the amino groups. Several of the bands observed in the 280–350 cm^{-1} region may be tentatively assigned to ν(M–N) and ν(M–X) vibrations by comparison of the spectra of free ligands with those of the complexes.

The electronic absorption spectra of yellow $[Ni(PHZ)_2](ClO_4)_2$ and $[Ni(PHZ)_2]SO_4$ complexes are typical of planar nickel(II), D_{2h} symmetry, with a strong maximum at 22,700 cm^{-1} independent of the solvent or anion [8]. The shape and the intensity of this band is identical to the band observed for other planar nickel(II) complexes [1, 3, 14, 15]. The magnetic and conductance properties of nickel(II)–PHZ complexes are also consistent with planar coordination around the nickel(II) atom. The single crystal X-ray structure determination [15 b] of $[Ni(PHZ)_2]$-$(ClO_4)_2$ shows that the structure consists of discrete $[Ni(PHZ)_2]^+$ cations (Fig. 1) and ClO_4^- anions which further confirms the planar geometry around nickel(II). Contrary to PHZ, the MPHZ forms green monocomplex, [Ni(MPHZ)Cl_2]. The solution spectrum (Fig. 1) of [Ni(MPHZ)Cl_2] shows a broad absorption at about 18,200 cm^{-1} with a shoulder around 16,660

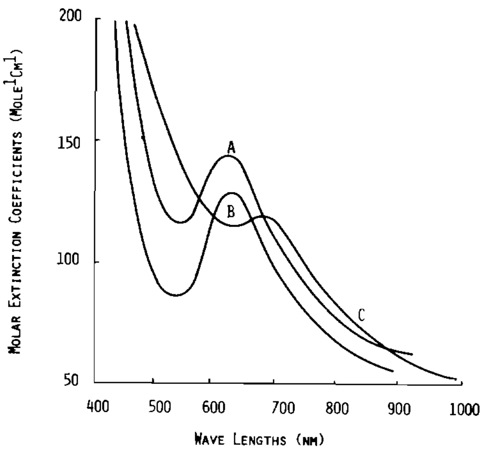


Fig. 3. Visible absorption spectra of Copper(II) complexes of MPHZ in nitromethane: (A) [Cu(MPHZ)Cl_2], (B) [Cu-(MPHZ)SO_4], (C) [Cu(MPHZ)Br_2]. The solid state spectra of all three compounds have absorption maxima at 620 nm (16,00 cm^{-1}).

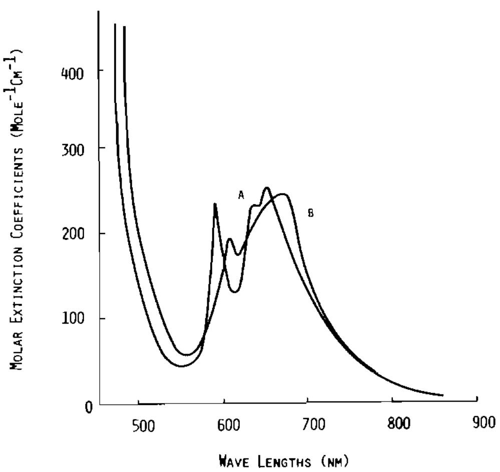


Fig. 4. Visible absorption spectra of MPHZ complexes of Cobalt(II) in nitromethane: (A) [Co(MPHZ)Cl_2], (B) [Co-(MPHZ)Br_2].

cm^{-1}, probably indicative of tetrahedral geometry [16] around the nickel(II) atom. The magnetic moment of 2.99 B.M. and the non-electrolytic behaviour of this complex are consistent with distorted tetrahedral symmetry of nickel(II) atom in [Ni(MPHZ)-Cl_2] as compared to the diamagnetic [Ni(PHZ)$_2$]·(ClO_4)$_2$.

The electronic spectra of mono- and bis-PHZ complexes of copper(II) have been explained earlier [8] The conductance and spectral data support tetragonally distorted octahedral copper(II) complexes when anions are nitrate or chloride. In the case of [Cu(PHZ)$_2SO_4$], the absorption maximum (Fig. 2) observed at 18,200 cm^{-1} both in the solid state and in nitromethane solution is similar to the pentacoordinated [Cu(dach)$_2$Cl]ClO_4 complex [17, 18]. The complex is non-electrolytic in behavior with the i.r spectrum showing monodentate sulfate ion with absorption peaks at 1110, 1010 and 605 cm^{-1} [19]. The electronic absorption spectra of mono-complexes of MPHZ exhibit a single absorption peak in the region 14,000–16,000 cm^{-1} (Fig. 3). The blue or green color of the complexes are due to the presence of an absorption band in the region 13,000–15,000 cm^{-1} [20]. The envelopes of these bands are generally unsymmetrical seeming to encompass several overlapping transitions. The single band observed at 15,850 cm^{-1} for Cu(MPHZ)X_2/SO_4 is in contrast to the strong band observed at 19,950 cm^{-1} for [Cu-(daco)$_2$](ClO_4)$_2$ [1], which has a distorted octahedral geometry, but is similar to the absorption maximum at 16,100 cm^{-1} observed in the case of [Cu(daco-diac)$_2$]X_2 [21]. The decrease in absorption band energy may be attributed primarily to the degree of axial perturbation which depends upon the specific steric requirements of the ligands under investigation.

Attempts to complex cobalt(II) with PHZ were not successful. However, green [Co(MPHZ)Cl_2] and [Co(MPHZ)Br_2] with magnetic moments of 4.00 B.M. and 4.05 B.M. respectively were synthesized.

TABLE III. Proton Nuclear Magnetic Data for PHZ and MPHZ Complexes (ppm in DMSO-d_6)*.

Compound	$\delta H_{C_6H_5}(6H)^a$ (m)	$\delta NH(2H)^b$ (bs)	$\delta CH_2(4H)^c$ (bd)	$\delta N{-}CH_3(3H)^d$ (bs)	$\delta CH_3(6H)^e$ (s)
PHZ	6.59	5.61	4.29	–	2.05
MPHZ	6.67	5.68	4.29	3.10	2.10
Ni(PHZ)$_2$(ClO_4)$_2$	6.67	5.29	4.30	–	2.16
Pd(PHZ)$_2Cl_2$·2HCl	6.67	5.20	4.30	–	2.18
Pt(PHZ)Cl_2·2HCl	6.67	5.15	4.50	–	2.18
Pd(MPHZ)Cl_2·2HCl	7.00	5.43	4.33	3.03	2.17
Pt(MPHZ)Cl_4·2HCl	7.10	5.30	4.40	2.80	2.15

*m = multiplet; S = singlet; bs = broad singlet; bd = broad doublet. ^{a}= phenyl-H, ^{b}= amine-H, ^{c}= methylene-H, ^{d}= methylamine-H, ^{e}= methyl-H.

TABLE IV. Thermogravimetric Analyses of PHZ and MPHZ Complexes*.

Complex	Initial Wt. (mg)	Evapor. Moiety/ Temp. Range °C	Wt. Loss (mg)	Evapor. Moiety/ Temp. Range °C	Wt. Loss (mg)	Residue (mg)	
$Cu(PHZ)Cl_2$	45.00	2PHZ 250–450	28.00 (28.79)	–	–	$CuCl_2$	16.00 (16.20)
$Cu(PHZ)Br_2$	40.00	2PHZ 200–450	20.50 (20.65)	–	–	$CuBr_2$	19.00 (19.34)
$Cu(PHZ)_2SO_4$	64.45	PHZ 200–300	24.00 (24.20)	$PHZ + SO_3$ 350–450	32.00 (31.00)	CuO	8.00 (8.00)
$Ni(PHZ)_2SO_4$	45.20	PHZ 200–400	17.00 (17.30	$PHZ + SO_3$ 400–650	21.50 (91.96)	NiO	5.70 (5.60)
$Zn(PHZ)_2Br_2$	56.50	PHZ 250–380	18.50 (19.20)	PHZ 550–700	19.50 (19.20)	$ZnBr_2$	17.90 (17.90)
$Pd(PHZ)_2Cl_2 \cdot 2HCl$	71.00	$2HCl + Cl_2$ 150–250	13.00 (13.5)	2PHZ 300–400	44.95 (39.50)	PdO	
$Pt(PHZ)_2Cl_4 \cdot 2HCl$	36.40	$2HCl + Cl_2$ 150–250	9.00 (8.84)	2PHZ 300–400	19.00 (19.5)	PtO	7.80 (8.6)
$Pt(PHZ)Cl_2$	40.00	PHZ 200–400	18.98 (18.88)	Cl_2 400–500	5.90 (5.6)	PtO	15.50 (16.74)
$Co(MPHZ)Cl_2$	36.30	Cl_2 200–300	10.00 (6.70)	MPHZ 350–400	18.00 (23.90)	CoO	8.00 (5.2)
$Co(MPHZ)Br_2$	26.30	Br_2	8.50 (8.9)	MPHZ 400–450	14.00 (14.10)	CoO	3.00 (2.3)
$Co(MPHZ)Cl_2$	34.30	MPHZ 250–350	23.00 (22.18)	–	–	$NiCl_2$	11.30 (12.1)
$Cu(MPHZ)Cl_2$	20.50	MPHZ 200–350	13.40 (13.38)	–	–	$CuCl_2$	7.40 (7.12)
$Cu(MPHZ)SO_4$	11.25	SO_3 200–280	22.00 (22.50)	MPHZ 350–450	66.50 (67.5)	CuO	21.75 (21.11)
$Zn(MPHZ)Br_2$	23.00	MPHZ 250–350	12.00 (12.15)	–	–	$ZnBr_2$	10.50 (10.85)
$Pd(MPHZ)Cl_2 \cdot 2HCl$	31.20	$2HCl + Cl_2$ 150–300	9.00 (9.0)	MPHZ 300–450	14.00 (14.6)	PdO	8.20 (7.07)
$Pt(MPHZ)Cl_4 \cdot 2HCl$	18.60	$2HCl + Cl_2$ 150–250	6.00 (5.98)	MPHZ 300–400	7.20 (7.08)	PtO	5.40 (5.9)
$Pt(MPHZ)_2Cl_2$	24.25	–	–	$MPHZ + Cl_2$ 350–500	18.00 (18.11)	PtO	6.00 (6.64)

*Calculated weight loss in mg is given in parentheses. In all cases a heating rate of 5 °C/min was used.

The visible spectra of cobalt(II) complexes of MPHZ (Fig. 4) exhibit three absorption maxima between 14,000 to 17,000 cm^{-1}. The first set of bands could be assigned to $^4A_2(F) \rightarrow {}^4T_1(P)$ transition [22]. The spectra of $[Co(MPHZ)Cl_2]$ and $[Co(MPHZ)Br_2]$ are identical to those of $[Co(daco)Cl_2]$ and $[Co(dach)Br_2]$ which are assigned a distorted tetrahedral geometry [2].

Attempts to synthesize mono-complexes of the type $[Zn(PHZ)X_2]$ were not successful and only non-electrolytic bis-complexes of PHZ of the type $[Zn(PHZ)_2X_2]$ were formed. The MPHZ, on the other hand, formed only mono-complexes with Zinc(II). In view of the well known tendencies of Zinc(II) to form tetrahedral complexes, $[Zn(MPHZ)Br_2]$ may be considered to have tetrahedral geometry with MPHZ acting as bidentate whereas in $[Zn(PHZ)_2X_2]$ the PHZ would be monodentate. The tetrahedral geometry of Zn(II) complexes of both PHZ and MPHZ is consistent with the i.r. spectra and non-electrolytic behavior of the complexes.

The complexes of palladium(II) or platinum(II) have not been reported for any mesocyclic ligands nor for their modified forms, except for a palladium complex of piperazine [23]. Both PHZ and MPHZ form non-electrolytic crystalline $[Pd(PHZ)_2Cl_2] \cdot 2HCl$ and $[Pd(MPHZ)Cl_2] \cdot 2HCl$ when the solution of palladium(II) chloride with a small amount of HCl was mixed with the ligands. The solid state spectra of both palladium complexes gave a weak maximum at about 16,000 cm^{-1} which resembles a transition at 16,250 cm^{-1} in square-planar $PdCl_4^{2-}$.

TABLE V. Magnetic and Conductance Data for PHZ and MPHZ Complexes*.

Compound	Cor. 10^{-6} χ_m, cgsu	μ_{eff}^{a} B.M.	Molar Conductance^b cm^2 ohm^{-1} mol^{-1}	Comments
$Cu(PHZ)_2(ClO_4)_2$	1115	1.80	27	non-electrolyte
$Cu(PHZ)_2SO_4$	1230	1.80	24	non-electrolyte
$Pd(PHZ)_2Cl_2 \cdot 2HCl$	212	dia	25	non-electrolyte
$Pt(PHZ)_2Cl_2 \cdot 2HCl$	347	dia	23	non-electrolyte
$Pt(PHZ)_2Cl_2 \cdot 2HCl$	253	dia	58	non-electrolyte
$CO(MPHZ)Cl_2$	6566	4.00	17	non-electrolyte
$CO(MPHZ)Br_2$	6705	4.05	25	non-electrolyte
$Cu(MPHZ)Cl_2$	1307	1.78	18	non-electrolyte
$Cu(MPHZ)Br_2$	1111	1.70	24	non-electrolyte
$Cu(MPHZ)SO_4$	1203	1.72	29	non-electrolyte
$Ni(MPHZ)Cl_2$	3654	2.99	29	non-electrolyte
$Pd(MPHZ)Cl_2 \cdot 2HCl$	–	dia	27	non-electrolyte
$Pt(MPHZ)_2Cl_2$	–	dia	112	1:2 electrolyte
$Pt(MPHZ)Cl_4 \cdot 2HCl$	–	dia	25	non-electrolyte
$Ni(PHZ)_2(ClO_4)_2$	244	dia	150	1:2 electrolyte
$Ni(PHZ)_2SO_4$	223	dia	80	1:1 electrolyte

$^a\mu_{eff} = 2.84\chi_m T$ B.M., Diamagnetic correction values were approximated from values given in ref. 13. ^{b}Molar conductance was measured in nitromethane using solutions of 2.0×10^{-3} to 5.0×10^{-3} molar concentration.

The platinum(II) complex $Pt(PHZ)Cl_2 \cdot 2HCl$ was prepared in acidic medium. It was a non-electrolyte with two HCl molecules of crystallization. Platinum(IV) also formed non-electrolytic diamagnetic, $Pt(PHZ)_2Cl_4 \cdot 2HCl$. The MPHZ forms the bis-complex $Pt(MPHZ)_2Cl_2$, which is uni–bivalent in nitromethane while the mono-complex $Pt(MPHZ)Cl_4$ was non-electrolyte in the same solvent. The solid state or solution spectra of platinum complexes were inconclusive.

Thermogravimetric Analysis

The thermal stabilities of the PHZ complexes of nickel(II), copper(II), zinc(II), palladium(II) and platinum(II and IV) were studied by TGA techniques. In all these complexes dissociation occurs in a regular sequence but thermal stabilities differ significantly from one another, probably indicating differences in structures (Table IV).

In $[Ni(PHZ)_2]X_2$ complexes, where X stands for Cl^-, I^-, both ligand molecules are lost in the temperature range 200–300 °C leaving the corresponding metal halides as the residue. Vaporization of both the PHZ molecules simultaneously is an indication of the equivalence of PHZ moieties in the nickel(II) complexes. In the case of $[Ni(PHZ)_2](NO_3)_2$ one ligand molecule and N_2O_5 moiety are detached in the temperature range 200–350 °C. It is remarkable that the second ligand molecule stays on and vaporizes very slowly from 350–500 °C leaving metal oxide as the residue. The thermal behavior of $[Ni(PHZ)_2]So_4$ is different from that of $[Ni(PHZ)_2](NO_3)_2$ but similar to that of $[Cu(en)_3]SO_4$ [24]. The thermogram of $[Ni(PHZ)_2]SO_4$ shows that at a temperature of 200–400 °C only one ligand molecule vaporizes, while vaporization of the second molecule of PHZ and SO_3 occurs at 400–650 °C leaving behind metal oxide. The thermal behavior of nitrate and sulfate complexes of copper(II) and nickel(II) are similar, except for the difference in decomposition temperatures. In the mono-complexes of copper(II), $[Cu(PHZ)X_2]$, $X = Cl^-$, Br^-, only the ligand moiety is lost at 200–450 °C, leaving the metal halide as the residue.

In zinc(II) halide complexes $[Zn(PHZ)_2X_2]$, $X = Cl^-$, Br^-, first the PHZ molecule evaporates at the 250–350 °C, whereas the second PHZ moiety is lost in the range 350–500 °C. $[Zn(PHZ)_2(NO_3)_2]$ gives a heating curve similar to those of bis-PHZ complexes of nickel and copper.

The bis-complexes of palladium(II) and platinum(IV) have identical thermal behavior. These complexes began to lose weight at 150–250 °C with the detachment of two HCl molecules and two molecules of chlorine. Both molecules of PHZ vaporized at 300–400 °C. On further heating no change in weight was observed, and the residue corresponds to the oxides of the metal. The mono-complex of platinum(II) behaves differently. First the PHZ molecule evaporates at 200–400 °C and later a chlorine molecule is lost leaving the metal oxide.

Thermal behavior of MPHZ complexes in many cases was found to be different from that of PHZ. The cobalt(II)-MPHZ complexes began to lose weight at 200 °C and the loss in weight was completed at 450 °C. The loss of weight took place in two steps. In the first step X_2, $X = Cl$, Br was detached and vaporized, whereas in the second step the MPHZ molecule was lost leaving cobalt(II) oxide as the residue. The observed thermograms for the MPHZ complexes are best explained by the following mode of decomposition. No efforts were made to identify the evaporating moieties.

1. $M(MPHZ)X_2 \rightarrow MO + MPHZ + X_2$
   $M = Co(II)$
   $X = Cl^-, Br^-$
2. $M(MPHZ)X_2 \rightarrow MX_2 + MPHZ$
   $M = Ni(II), Cu(II), Zn(II)$
   $X = Cl^-, Br^-$
3. $Cu(MPHZ)SO_4 \rightarrow Cu + SO_3 + MPHZ$
4. $Pd(MPHZ)Cl_2 \cdot 2HCl \rightarrow PdO + MPHZ + Cl_2 + 2HCl$
5. $Pt(MPHZ)Cl_4 \cdot 2HCl \rightarrow PtO + MPHZ + 2Cl_2 + 2HCl$
6. $Pt(MPHZ)_2Cl_2 \rightarrow PtO + 2MPHZ + Cl_2$

Acknowledgements

M.S.H. is thankful to the University of Petroleum & Minerals, Dhahran, for providing research facilities where some parts of this work were completed. Thanks are also due to Mr. Martin Dawson for doing some spectral work and growing crystals of some compounds.

References

1 W. K. Musker and M. S. Hussain, *Inorg. Chem.*, *5*, 1416 (1966).
2 W. K. Musker and E. Steffen, *Inorg. Chem.*, *13*, 1951 (1974).
3 W. K. Musker and M. S. Hussain, *Inorg. Chem.*, *8*, 528 (1969).
4 M. S. Hussain and H. Hope, *Acta Crystallogr.*, *B25*, 1866 (1969).
5 W. K. Musker and N. L. Hill, *Inorg. Chem.*, *11*, 710 (1972).
6 a) D. O. Nielson, M. L. Larson, R. D. Willett and J. I. Legg, *J. Am. Chem. Soc.*, *90*, 5030 (1968); *93*, 5079 (1971).
b) M. H. West and J. I. Legg, *J. Am. Chem. Soc.,*, *98*, 6945 (1976).
7 B. N. Patel and E. J. Billo, *Inorg. Nucl. Chem. Letters*, *13*, 335 (1977).
8 M. S. Hussain and S. Rehman, *Z. Naturforsch.*, *336*, 67 (1978).
9 F. C. Cooper and M. W. Partridge, *J. Chem. Soc.*, 2888 (1957).
10 E. C. Wagner, *J. Chem. Soc.*, *57*, 1296 (1935).
11 R. H. Lee, E. Griswold and J. Kleinberg, *Inorg. Chem.*, *3*, 1278 (1964).
12 F. Danials, J. W. Williams, P. Bender, P. A. Alberty and C. D. Cornwell, 'Experimental Physical Chemistry', p. 158, 473, McGraw–Hill, New York, N.Y., 1962.
13 B. N. Figgs and J. Lewis, 'Modern Coordination Chemistry', p. 412, Interscience, New York, N.Y., 1960.
14 L. Sacconi, *Transition Metal Chem.*, *4*, 199 (1968).
15 a) B. Bosich, M. L. Tobe and G. A. Webb, *Inorg. Chem.*, *4*, 1109 (1965).
b) M. S. Hussain and E. O. Schlemper, unpublished results.
16 A. D. Liehr and C. J. Ballhauser, *J. Chem. Phys.*, *6*, 134 (1959).
17 W. K. Musker and M. S. Hussain, 'Progress in Coordination Chemistry', Michael Cais Ed., Elsevier, D32, 262 (1968).
18 W. K. Musker and M. S. Hussain, *Inorg. Nucl. Chem. Letters*, *3*, 271 (1967).
19 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', 2nd Edition, Wiley–Interscience, New York, 1970.
20 a) R. L. Belford, M. Calvin and G. Belford, *J. Chem. Phys.*, *26*, 1165 (1957).
b) J. Bjerrum, C. M. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, *8*, 1275 (1954).
21 F. Averil, J. I. Legg and D. L. Smith, *Inorg. Chem.*, *11*, 2344 (1972).
22 D. L. Wood and J. P. Pemeika, *J. Chem. Phys.*, *46*, 3595 (1967).
23 a) P. J. Hendra and D. B. Powell, *J. Chem. Soc.*, 5105 (1960).
b) F. G. Mann and H. R. Watson, *ibid.*, 2772 (1958).