Transition Metal Complexes of 2,8-Dimethyl-6H, 12 H-5, 11-Methanodibenzo [b,f] [1,5] diazocine

SAEED-UR-RAHMAN
Department of Chemistry, University of Peshawar, Peshawar, Pakistan.

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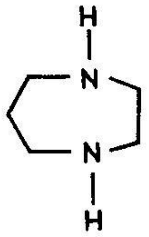
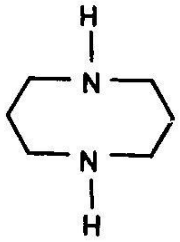
Summary: The titled compound (EPHZ) can be compared with 5:6:11:12-tetrahydro -2:8-dimethylphenhomazine (PHZ) and 5:6:11-trihydro-2:5:12-trimethylphenhomazine (MPHZ) in its structural characteristics on coordination to several transition metals. In EPHZ both the amines are bridged through the methylene group and thus providing more room for fifth and sixth coordination. EPHZ forms bis-complexes with cobalt(II), cooper(II), mercury(II) and cadmium(II). The molecular structure of these complexes is assigned on the basis of analytical, spectroscopic, magnetic, and conductance data. The thermogravimetric studies are reported and discussed. The ligand is characterized by its mass spectra.

Seven and eight membered-ring systems containing two donor atoms are known to confer various geometries to metal ions due to their specific steric requirements and unusual chelate bite angle. Maximum metal ligand stability is achieved through multiple five or six membered chelate ring fomration and/or due to effective shielding of the axial positions of the central metal ion when two eight membered rings function as chelating agents in chair/boat conformation. Any twisting or change in this conformation which opens the axial positions increases inter or intra ligand interaction within the molecule [1-3].

1,4-diazacycloheptane (dach) and 1,5-diazacyclooctane (daco), which are seven and eight membered cyclic diamines, form complexes with cabolt (II), nickel(II), and copper(II). The complexes of dach are penta-coordinated. The complexes of daco with copper(II) and nickel(II) are square-planar whereas with cobalt(II), they are five coordinated with anions strongly bonded at the apical position [4].



I. 1,4-diazacycloheptane. (dach)

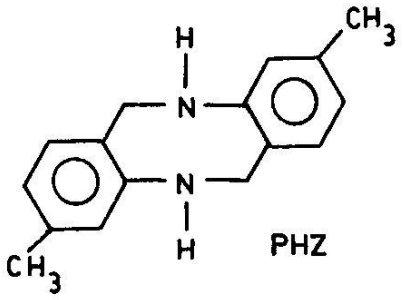


II. 1,5-diazacycloctane. (daco)

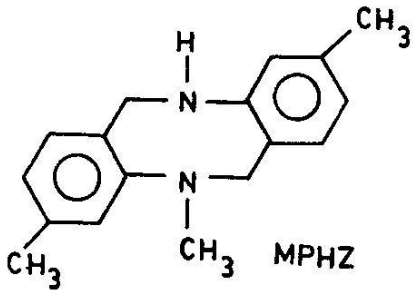
Modification of the cyclic diamines with acetate and ethylamine functions, prdouces tri-dentate daco-monoacetate, and tetradentate daco-diacetate [5-6]. In all known cases, chelation of medium ring diamines causes blocking of at least one axial position forbidding the formation of six coordinated complexes.

The cyclic amidines, 5:6:11:12-tetrahydro-2:8-dimethylphenhomazine (PHZ) and 5:6:11-trihydro-2:5:8-trimethylphenhomazine (MPHZ) can be viewed as eight-membered cyclic

diamine, with carbon atom pairs 3,4 and 7,8 of the daco forming part of benzene.



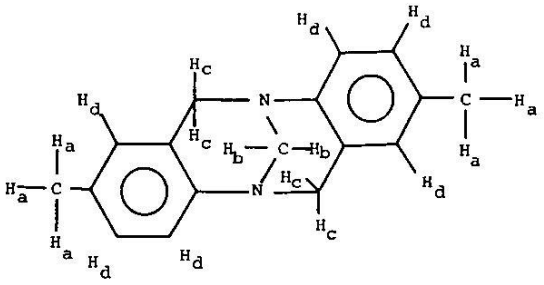
III. 5:6:11:12-Tetrahydro 2:8-dimethylphenhomazine



IV. 5:6:11-Trihydro-2:5:8 trimethylphenhomazine.

It is seen that the flexibility of daco to attain boat-boat, boat-chair or chair-chair conformation is somewhat reduced by the presence of bulky benzene rings, thus opening the axial positions for further coordination. In addition to six coordinated complexes, they also form four coordinated complexes, indicating that the blocking of axial position is not the only factor forcing exclusive formation of four and five coordinated complexes [7,8].

The present investigations were carried out to study the effect of steric hindrance on the geometry of the complexes. The ligand 6:12-dihydro-2:8-dimethyl-5:11-endomethylenephenhomazine (EPHZ)* was chosen because hydrogen (s) of the amines are replaced by endomthylene bridge. Thus it provides more room for fifth and sixth coordination through apical positions. Further the coordination space also increased the steric hinderance of the molecues.



V. 6:12-dihydro-2:8-dimethyl-5:1-11-endomethylene phenbomazine (EPHZ).

In this paper, an attempt has been made to elucidate and explain the molecular structure of the complexes under report. Further, the properties of PHZ complexes have been compared with those of daco, PHZ and MHPZ complexes.

Experimental

Materials

Metal salts were obtained from E. Merck and were used without further purification. Dehydration was achieved by shaking the salts with 2,2-dimethoxypropane for at least four to five hours [9]. The purity of salts was checked by usual methods. The non aqeuous solvents which were used for syntheses and spectral analyses were properly dried and distilled twice before use.

Ligand

The ligand (EPHZ) was prepared by the method and conditions suggested by Wagner [10], except that the

*EPHZ : 2,8-Dimethyl-6H, 12 H-5, 11-Methanodibenzo [b,f] [1,5] diazocine.

hydrochloride was isolated as recommended by Cooper and Partidge [11]. The product was dried and recrystallized from ethanol

Mp 137°C (lit. [11] mp 136-7°C. Anal. Calcd. for $C_{17}H_{18}N_2$, C, 81.70 H, 7.20; N, 11.20% Found C, 81.65; H, 7.24; N, 11.21%.

Preparation of the Complexes and Analytical Data (Table 1)

The metal ion and ligand solutions were deaerated with pre-purified nitrogen and all subsequent operations were formed on a vacuum line under nitrogen atmosphere. The ligand solution was added slowly while stirring. The solid complexes formed on mixing the two solutions or upon reducing the volume of the mixture. The complexes were isolated by filtration under vacuum, washing with ether and drying at 105°C for 3-4 hrs.

Magnetic Susceptibility Measurements (Table-2)

The magnetic moments of the solid complexes determined by the Gouy method, at room temperature. A double ended Gouy tube was calibrated using $Hg[Co(NCS)_4]$ as the standard. Pascal's constants were used to correct the observed molar susceptibilities of crystalline complexes for the diamagnetism of the ligand and the anions involved [12].

Electrolytic Conductance Measurements (Table-2).

The electrolytic conductance measurements of the complexes were made on the conductivity bridge by Mullard, Inc. England. The conductivity cell was calibrated [13], and the observed conductivities were corrected for the specific conductance of the pure solvent used.

UV and Visible Spectra (Table-3)

Visible and ultraviolet spectra of the complexes in different solvents were obtained with a JASCO UNIDEC-1 recording spectrophotometer using a set of matched 1-cm quartz cells. The absorption spectra were always recorded using freshly prepared solutions. The solid state spectra were also measured by placing filter paper soaked in Nujol Mull of the complexes, into the beam of the spectrophotometer.

Infrared Spectra (Table-4)

The infrared absorption spectra of the solid complexes were obtained with a JASCO IR-I and a Beckman IR 2440 spectrophotometers. The IR were examined in Nujol Mull supported on NaCl, KBr plates. In some cases, the spectra were measured using KBr Pallets.

Nuclear Magnetic Resonance Spectra (Tabl-5)

The NMR data for the ligand and few of its diamagnetic complexes were obtained in deuteriochloroform ($CDCl_3$) with a JNM-PMX 60 spectrometer. Tetramethylsilane (TMS) was used as an external standard.

Thermogravimetric Analysis (Table-6)

TGA of the complexes was done on a recording Stanton (England) thermogravimetric balance. Analytically pure anhydrous complexes were used and the measurements were made in triplicate for each complex.

Table-1: Analytical data for EPHZ Complexes

Compound	Mp °C	Colour	C %	H %	N %	Metal %	Anion %
$Cu(EPHZ)_2Cl_2$	142	Red	64.80 (63.94)	5.64 (5.60)	8.52 (8.77)	10.02 (9.87)	11.58 (11.13)
$Cu(EPHZ)_2Br_2$	174	Brown	56.82 (56.12)	5.07 (4.95)	7.82 (7.70)	9.02 8.66)	21.82 (22.00)
$Cu(EPHZ)_2(NO_3)_2$	86	Green	60.40 (59.04)	5.02 (5.21)	12.60 (12.20)	9.08 (9.17)	- -
$Co(EPHZ)_2Cl_2$	173	Darkblue	64.68 (64.76)	5.90 (5.72)	9.24 (8.88)	8.62 (8.35)	11.36 (11.26)
$Hg(EPHZ)_2Cl_2$	167	White	52.32 (52.90)	4.88 (4.66)	7.59 (7.25)	25.33 (25.90)	9.95 (9.20)
$Hg(EPHZ)_2Br_2$	173	Dullwhite	47.80 (47.40)	4.33 (4.18)	6.73 (6.50)	22.92 (23.30)	17.87 (18.59)
$Hg(EPHZ)_2(NO_3)_2$	137	White	47.90 (49.48)	4.41 (4.36)	9.95 (10.18)	24.57 (24.34)	- -
$Cd(EPHZ)_2Cl_2$	297	Dullwhite	58.68 (59.73)	5.18 (5.27)	8.05 (8.19)	16.80 (16.45)	11.58 (10.38)
$Cd(EPHZ)_2Br_2$	228	White	52.80 (52.82)	4.66 (4.66)	7.25 (7.24)	14.40 (14.55)	21.33 (20.69)

Calculated values are given in parentheses.

Mass Spectral Measurements (Table-7)

The mass spectra of the ligand was obtained with VG-Micromass 12 Spectrometer.

Discussion

Analytical Data

Analytical data (Table-1) of EPHZ complexes show that EPHZ forms bis-complexes with cobalt(II), copper(II), mercury(II) and cadmium(II). The elemental analysis of the EPHZ complexes are reported in the Table-1.

Spectroscopic, Magnetic and COnductance Studies

The cobalt(II) complexes EPHZ has a magnetic moment of 4.8 B.M, being paramagnetic with three unpaired electrons. The conductance data give no ionic character, so the complex may be assigned a distorted tetrahedral

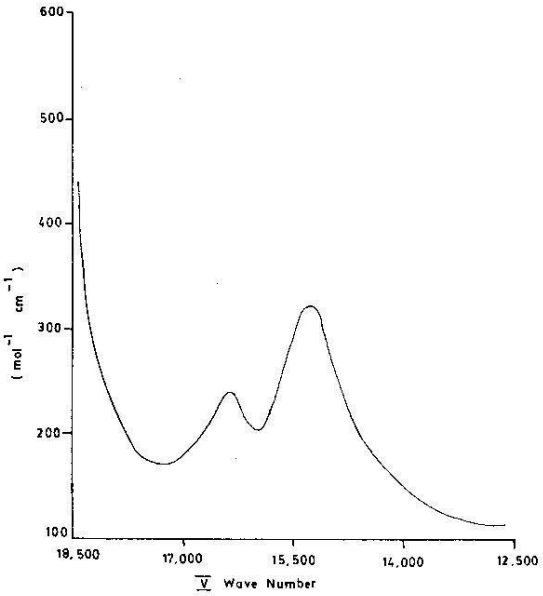


Fig.1: Visible Absorption Spectra of $Co(EPHZ)_2Cl_2$

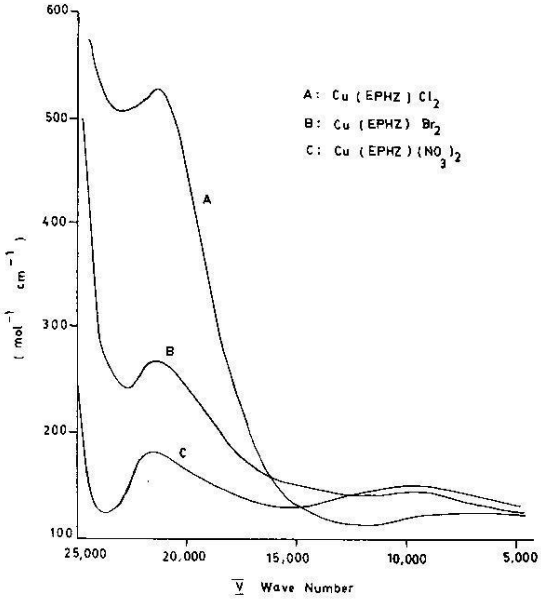


Fig.2: Visible Absorption Spectra of Copper (I) Complexes of EPHZ.

geometry. This assumption is further supported by the visible spectra (Fig. 1). The electronic absorption spectra of Co $(EPHZ)_2Cl_2$ is very similar to $CoCl_4^{-2}$ and $Co(dacoda)H_2O$ in solution form [14]; which are tetrahedral in geometry. The transitions are assigned from $^4A_2$ to $^4T_1(P)$ and $^4T_1$ (F). Further the IR spectra shows that nitrogen-carbon vibration splits up into two bands one remaining at its original position and the other one being shifted shwoing two types of nitrogen-carbon vibration, one due to attachment of nitrogen in the metal, where the other is free.

The cobalt(II) complex of EPHZ are like those of daco. Both these ligands impart a tetrahedral geometry. PHZ does not form complexes with cobalt(II).

The magnetic moment of $Cu(EPHZ)X_2$, where X stands for Cl, Br, and NO_3, ranges from 1.7 to 1.8 B.M; which are very close to the spin only value for the unpaired electron. The conductance behaviour shows, that complexes are non electrolytic in nature. The spectral curves of copper (II) complexes are symmetric with a very high extinction coefficient values from 530-550 at 470 nm. This spectrum is very much similar to that of $[Cu(dach)_2Cl]Cl$ [1-3].

In fact no significant conclusion can be drawn from magnetic moment values. However spectral measurements suggest the square pyramidal geometry [3] in solution state. The same pattern of IR spectra is observed as that in case of cobalt(II) complexes.

The structural characteristics of copper(II) complexes with EPHZ are very much different from those of PHZ and MPHZ compelxes. The latter are either distorted octahedral or penta-coordinated in solid state.

No complexes of cyclic amidines or cylic diamines with cadimum(II) or mercury(II) are reported so far. The complexes of cadmium(II) and mercury (II) with EPHZ are diamagnetic and

non electrolytic in nitromethane. The complexes of PHZ and MPHZ with zinc (II), which is the member of the same group, are tetrahedral in nature. Keeping in view the well knwon tendencies of the group, the same structure may be proposed for $Cd(DPHZ)_2X_2$ and $Hg(EPHZ)_2X_2$. This

Table-2: Magnetic and Conductance data of EPHZ Complexes

Compound	M* (mho $mol^{-1}cm^2$)	$10^6 \times \chi^{cor}_m$ (cgsu)	μ eff (B.M.)
$Co(EPHZ)_2Cl_2$	13 Non-Elect.	1225	4.865
$Cu(EPHZ)_2Cl_2$	15 Non-Elect.	414	1.75
$Cu(EPHZ)_2Br_2$	9 Non-Elect.	733	1.70
$Cu(EPHz)_2(NO_3)_3$	19 Non-Elect.	544	1.80
$Cd(EPHZ)_2Cl_2$	7 Non-Elect.	-	diamagnetic
$Cd(EPHZ)_2Br_2$	13 Non-Elect.	-	-do-
$Hg(EPHZ)_2Cl_2$	3 Non-Elect.	-	do-
$Hg(EPHZ)_2Br_2$	0 Non-Elect.	-	-do-
$Hg(EPHZ)_2(NO_3)_2$	15 Non-Elect.	-	-do-

*Electrolytic conductance was measured in nitromethane and DMSO at 10^{-3}M at 25°C. Magnetic moments were measured in solid state by Guoy Method.

Table-3: Electronic Absorption Data of EPHZ Complexes

Complex	Solvent	λnm	$\nu_{cm^{-1}}$	max	Comments
$Co(EPHZ)_2Cl_2$	CH_3NO_2	610	16.400	240	$^4A_2 \rightarrow {}^4T_1$ (P)
		665	15.00	320	$^4A_2 \rightarrow {}^4T_1$ (F)
Co(dacoda)H_2O	D_2O	450	22.22	22	do
		560	18,00	32	do
$CU(EPHZ)_2Cl_2$	CH_3NO_2	470	21.000	530	d---d trans.
$Cu(EPHZ)_2Br_2$	-do-	465	21,000	230	do
$Cu(EPHZ)_2(NO_3)_2$	-do-	465	21.500	120	do

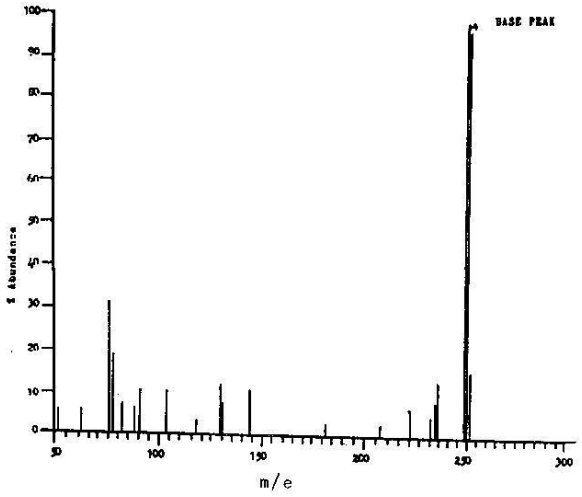


Fig.3: Mass Spectrum of 6:11-dihydro-2:8-dimethyl,5:12-endomethylenephenhomazine.

assumption is also supported by IR spectra, which show attachment of only one nitrogen of the ligand.

Infrared Spectral Analysis of EPHZ Complexes

A summary of IR bands of the solid complexes in Nujol Mull, in the selected region, has been given in the Table-4. The infrared spectrum of EPHZ has a sharp band at 1180 cm^{-1} assigned to C-N vibration. In metal complexes, this band either shifts to higher frequency or becomes broad or splits up into two or three, suggesting coordination through this nitrogen. Contrary to PHZ and MPHZ a strong band at 1610 cm^{-1} does not appears.

In cobalt(II) complexes, the C-N vibration frequency splits up into two bands at 1150 and 1170 cm^{-1}. Infrared spectrum of nitrate derivatives contained bands, that can be assigned both to ionic and unidentate nitrate groups. The $Hg(EPHZ)_2(NO_3)_2$ and $Cu(EPHZ)_2(NO_3)_2$ exhibit two bands at 980 and 1310 cm^{-1} which can be assigned to unidentate nitrate group as these bands are absent in respective complexes with halides. If the nitrate group was to be ionic (D_{3h}), its IR spectrum would have bands at 1050, 1380, 830 and 720 cm^{-1} corresponding to N-O stretching, NO_2 stretching N-O bending and NO_2 bending modes [15]. No such bands were observed, showing no ionic NO_3 species. The IR spectra of $Hg(EPHZ)_2X_2/Cd(DPHZ)_2X_2$ complexes show one band at 1180 cm^{-1} was observed indicating the presence of both coordinated and uncoordinate groups.

NMR Spectral Analysis

Proton nmr data of the ligand EPHZ and its diamagnetic complexes are reported in Table-5. The nmr spectrum reveals that there are four different peaks corresponding to different protons attached to various moities. The singlets appear at 2.08 and 4.4 ppm, the doublet appear at 4.13 ppm and the multiplet is centered at 6.72 ppm (relative to external TMS=0). The peaks can be assigned to six protons of methyl groups attached to benzene rings, two protons of endomethylene bridge, four protons of methylene moieties and six protons of benzene moieties respectively. The nmr spectra of the complexes show only slight change in chemical shift values of endomethylene bridge, at least pointing coordination through $N-CH_2-N$ moiety. The ratio of the integrated intensities of various peaks agrees well with the calculated ratio of number of protons of various kinds.

Thermogravimetric Analysis

The thermal stabilities of the solid complexes were studies by thermogravimetric technqiues. In all these complexes, dissociation occurred in a

Table-4: Significant bands in the IR Spectra of EPHZ and its Complexes

Compound	νC-N (Stech)	IR Anions
EPHZ	1180 s	
$Co(EPHZ)_2Cl_2$	1160s, 1180 m,	
$Cu(EPHZ)_2Cl_2$	1160s, 1180 m,	
$Cu(EPHZ)_2Br_2$	1180 m	
$Cu(EPHZ)_2NO_3)_2$	1160 m	980 vs, 1310 vs
$Hg(EPHZ)_2Cl2$	1170s, 1100 s	
$Hg(EPHZ)_2Br_2$	1160s, 1180s	
$Hg(EPHZ)_2 (NO_3)_2$	1160 s, 1180 s	980 vs, 1310 vs
$Cd(EPHZ)_2$ Cl	1160 m, 1180 s	
$Cd(EPHZ)_2$ Br	1160 m, 1180 s	

different pattern showing that their stabilities differ significantly and so do their structures.

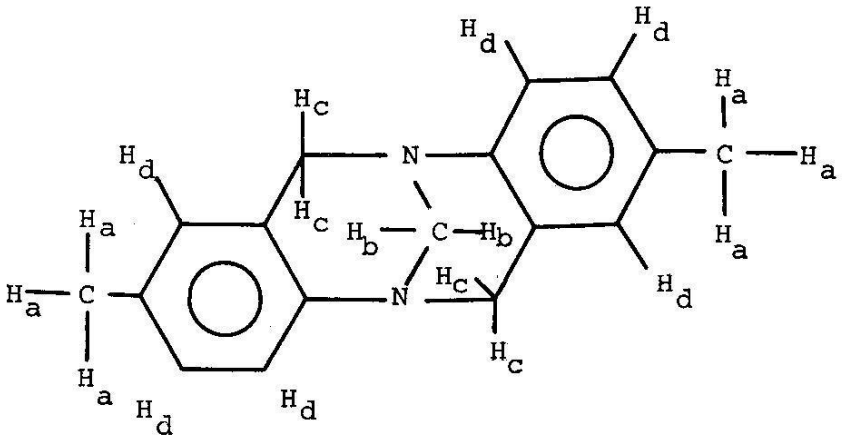
From the decomposition pattern and calcualted weight loss for the bis-complexes of EPHZ with cobalt(II) chloride at first step, the cleavage of one molecule of EPHZ was observed from 120°C to 510°C leaving behind $Co(EPHZ)Cl_2$ as a residue. This can be attributed to the higher stability of mono-complex.

In case of $Cu(EPHZ)_2X_2$ where X stands for Cl^- and Br^-, the halides were lost in first step in the temperture range 100-360°C. In the second step, EPHZ was lost in the range 320-640°C, leaving CuO as a residue. Vaporization of the ligand moieties at the same temperature indicates the equivalence of EPHZ entities in the complexes.

The weight loss curve indicated the emanation of one mole of nitrogen pentoxide (Temp. 95-110°C) per mole of the mono-Cu(II) nitrate complex in the first step. Elimination of the EPHZ was affected in the second step from 180 to 340°C leaving CuO behind as the remnant.

Bis-complexes with mercury and cadmium decomposed in an opposite sequence to the copper complexes as discussed above. Remarkably slow evaporation of the two ligand molecules from the complexes of mercury and cadmium was observed over a tempera-

Table-5: Nuclear Magnetic Resonance Data of EPHZ and its Complexes



CH_3 (6H)[a]	CH_2(4H)[c]	N-CH_2-N(2H)[b]	C_6H_3(6H)[d]
s ppm	bd ppm	bs ppm	m ppm
2.08	4.13	4.4	6.72 EPHZ
2.08	4.1	4.2	6.72 Cd(EPHZ)
2.08	4.08	4.3	6.70 Hg (EPHZ)

bd = broad doublet; bs = broad singlet; m=multiplet; s=singlet.

ture range of 140-680°C. Cadmium (II) bromide complex behaved slightly differently. The two EPHZ molecules were cleaved in two different steps. The vaporization of the second molecule took place at higher temperature.

The mercury(II) nitrate complex decomposed in a similar way to that of copper(II) nitrate complex except for the higher stability of the former.

A well agreed theoretical and calculated molar weight loss was found for all the above mentioned complexes.

The thermal behaviour of the complexes may be summarized by the following set of equations.

$$Co(EPHZ)_2Cl_2 \longrightarrow Co(EPHZ)Cl_2 + EPHZ$$

$$Cu(EPHZ)_2X_2 \longrightarrow CuO + 2\ EPHZ + X_2$$

X = Cl, Br

$$Cu(EPHZ)_2(NO_3)_2 \longrightarrow CuO + 2EPHZ + N_2O_5$$

$$M(EPHZ)_2X_2 \longrightarrow MO + 2EPHZ + X_2$$

Table-6: Thermogravimetric Data of EPHZ Complexes

Compound	Temp. rang Initial weight (mg)	100-35 0°C Evapor. moiety	Wt. Loss (mg)	350-500 °C Evaport. moiety.	Wt. loss (mg)	500-600°C Residue	(mg)
$Co(EPHZ)_2Cl_2$	28.9	EPHZ	12.82 (11.4)	-	-	$Co(EPHZ)Cl_2$	18.2 (17.4)
$Cu(EPHZ)_2Cl_2$	73.0	Cl_2	8.50 (8.12)	2EPHZ	57.50 (57.66)	CuO	9.50 (9.15)
$Cu(EPHZ)_2Br_2$	32.7	Br_2	8.15 (7.24)	2EPHZ	22.5 (22.61)	CuO	3.5 (3.5)
$Cu(EPHZ)_2(NO_3)_2$	80.0	N_2O_5	13.00 (12.70)	2EPHZ	59.00 (58.80)	CuO	9.30 (9.29)
$Cd(EPHZ)_2Cl_2$	38.7	2EPHZ	29.0 (28.3)	-	-	$CdCl_2$	11.00 (10.30)
$Cd(EPHZ)_2Br_2$	30.9	EPHZ	10.3 (10.3)	EPHZ	10.5 (10.3)	$CdBr_2$	11.4 (10.8)
$Hg(EPHZ)_2Cl_2$	24.0	2EPHZ	15.0 (15.6)	-	-	$HgCl_2$	10.2 (8.4)
$Hg(EPHZ)_2Br_2$	38.3	2EPHZ	22.00 (22.3)	-	-	$HgBr_2$	16.5 (15.96)
$Hg(EPHZ)_2(NO_3)_2$	45.3	N_2O_5	7.40 (6.45)	2EPHZ	27.50 (27.57)	HgO	12.00 (11.8)

Calculated weight loss in given in the parentheses.
A heating rate of 5°C/min was used.

Table-7: Mass Spectrum of 6:11-dihydro-2:8-dimethyl-5:11-endo-methylene phenhomazine

m/z	% abundance	m/z	% abundance	m/z	% abundance
51	6.0	103	13.8	178	2.0
52	4.0	105	10.0	192	1.8
57	2.4	107	2.0	194	4.0
63	5.8	109	2.2	206	1.2

Table-7 Contd.

m/z	% abundance	m/z	% abundance	m/z	% abundance
65	8.2	110	4.0	207	4.0
66	1.0	115	2.8	219	4.8
71	2.0	116	4.8	220	6.0
76	2.0	117	16.0	222	8.0
77	31.0	120	25.2	232	3.8
79	20.0	122	2.0	233	6.0
83	9.0	123	2.0	234	9.8
85	6.0	125	6.0	235	14.0
89	6.2	130	12.0	236	2.8
90	4.0	131	14.0	247	1.0
91	11.9	132	9.8	249	100.0
92	2.0	143	2.0	250	83.0
96	2.0	144	12.0	251	18.0
102	4.0	165	1.0	-	-

M = Cd, Hg

X = Cl, Br

$$Hg(EPHZ)_2(NO_3)_2 \longrightarrow HgO + 2EPHZ + N_2O_5$$

Conclusion

Results showed that the steric requirements play an important role towards the stability of the complexes and complexation. The endomethylene bridge makes it impossible sterically to coordinate as a bidentats ligand.

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