The Coordination ability of 1,3-Dipiperidinoe Propane Towards Transition and Representative Metals

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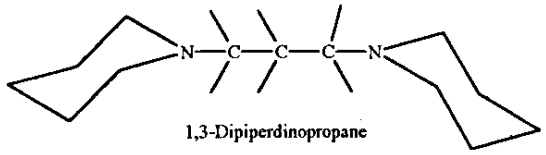
(Received 11th December, 1997, revised 22nd November, 1999)

Summary: 1,3-Dipiperidinoepropane (DPP), which can be viewed as N-substituted propylenediamine reacts with divalent first row transition and representative metals to give complexes of the stoichiometry, MLX_2 when L=DPP, M= Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Hg(II), while X= Cl^-, Br, I^- and NO_3^-. These complexes have been characterized by elemental analysis, conductivity measurements, room temperature magnetic moment studies, electronic and IR spectra. The ligand in these complexes behaves as bidentate like substituted propylenediamine coordinating through nitrogen atoms. The solid state IR study and other data support distorted tetrahedral geometry of the type MN_2X_2.

Introduction

Metal complexes, where coordination can occur between a variety of metal ions and a wide range of ligands play an important role in many biological systems [1,2]. It has been observed that metal ions have considerable effect on the antimicrobial activity of antibiotics [3-13]. Similarly metal complexes are known for their antitumour activity [14-18]. Our present work is of the same nature and concerns with the coordinating ability of 1,3-Dipiperidinopropane (DPP) [1]. a biologically active molecule.



1,3-Dipiperdinopropane

The ligand has been used as a neurotoxic agent due to vivo conversion to a selective cholinesterase inhibitor. Administration products seizures and central nervous system lesions. Also cholinergic origin of DPP toxicity has long been investigated. It is both an acetylcholinesterase (AChE) inhibitor and

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muscarinic antagonist. This dual action negates most of the toxic effects of the compound in vivo. The neurotoxicity is believed to arise from oxidative conversion to 1-N oxide which selectively inhibits AChE. Since binding parameters were unchanged following in vivo exposure, cytotoxicity does not involve muscarinic neurons [19]. Inspite of considerable importance of this molecule no work has been done on the synthesis of metal complexes of this ligand in solid state. Therefore, present work was undertaken with specific view to synthesize, isolate, and characterize solid complexes of transition and representative metals with 1,3-Dipiperidinopropane. The structural assignments have been justified by magnetic, conductance, analytical, UV-Visible and IR data.

Results and Discussion

Several complexes of 1,3-Dipiperidinopropane with the first row transition and representative metals have been synthesized and studied. The characterization and assignment of their geometry was based on the elemental analysis, conductance measurements, magnetic susceptibilities and spectral measurements. The infrared spectrum of DPP showed C-H and C-N stretching vibrations in the range 2965-2870 cm^{-1} and 1225-1085 cm^{-1} respectively. A mass peak of moderate intensity at m/z 210, corresponding to the molecular ion $(C_{13}H_{26}N_2)^+$ was observed in the spectrum of DPP. The base peak of m/z 98 is due to the formation of N-methylpiperidine cation radical, while the signals at m/z 112, 126 and 84 could be assigned to N-ethylpiperidine, N-propylpiperidine and piperidine respectively. The ligand DPP behaves as a bidentate ligand and bears resemblance to 1,3-dimorpholinopropane (DMP) in terms of chromophobic environment [20-22]. The complexes are soluble in DMSO. Representative metal complexes are also soluble in acetone and some in nitromethane whereas transition metal complexes are slightly soluble in these solvents.

The characteristic bands in the infrared spectra of DPP and its metal complexes are given in Table-3. The infrared spectrum of the free ligand, DPP in KBr exhibits a strong absorption band at 1148 cm^{-1} and a shoulder at 1117 cm^{-1}. These bands are assigned to C-N stretching vibrations [30-31].

The $[Zn(DPP)Cl_2]$, $[Zn(DPP)Br_2]$ and $[Zn(DPP)(NO_3)_2]$ complexes have strong band at 1148 cm^{-1} and a shoulder at 1117 cm^{-1} assigned to C-N stretching vibrations, is split into four distinct bands with the exception of $[Zn(DPP)(NO_3)_2]$ where three bands are observed. The strong band at 1148 cm^{-1} moves considerably to lower frequency side by about 35 cm^{-1} as compared to the free ligand and appeared at 1112 and 1115 cm^{-1} whereas the other two weak bands shift towards higher frequency side. In nitrate complex, a weak band at 1178 cm^{-1} and a shoulder at 1130 cm^{-1} were observed.

The $[Cd(DPP)Cl_2]$, $[Cd(DPP)Br_2]$ and $[Cd(DPP)(NO_3)_2]$ were synthesized. Similar complexes of Hg(II) were also isolated. In these complexes the bands attributed to C-N stretching vibrations like Zn(II) complexes is split into four bands with the exception of $Hg(DPP)(NO_3)_2$, where three bands were observed. The strong band observed at 1148 cm^{-1} in the free ligand suffers a red shift by 30 to 40 cm^{-1} and the other band moves to higher frequency side in comparison to the free ligand.

The behaviour of Cd(II) and Hg(II), DPP complexes is similar to Zn(II) complexes. The strong band at 1148 cm^{-1} shifts to lower frequency side.

Three complexes of Co(II), $[Co(DPP)Cl_2]$, $[Co(DPP)Br_2]$, and $[Co(DPP)(NO_3)_2]$ were synthesized and isolated in solid state. In all these complexes the bands attributed to C-N stretching vibrations is split into three distinct bands as compared to the free ligand.

The $[Ni(DPP)Cl_2]$, $[Ni(DPP)Br_2]$, and $[Ni(DP)(NO3)_2]$ behaves similar to Co(II) complexes. The bands at 1148 and 1117 cm^{-1} attributed to C-N stretching vibrations are split into three bands. Two move to higher frequency side and the other moves to lower frequency side. The strong band undergoes a red shift by 20-40 cm^{-1}.

Infrared spectra of metal complexes clearly indicate the C-N stretching frequencies are shifted to lower and some to higher frequencies with changes in sharpness and intensities. This is caused by the withdrawal of electron density from the C-N band where nitrogen atom become coordinated to the

Table-1: Analytical data for DPP and its metal complexes

Compound	Color	Dec.Pt. C	%C Found (Calc)	%H Found (Calc)	%N Found (Calc)	%Anion Found (Calc)	% Metal Found (Calc)
DPP(HBr) $C_{13}H_{26}N_2HBr$	Colorless	304	41.61 (41.65)	7.75 (7.58)	7.46 (7.53)	-	-
$Zn(DPP)Cl_2$	Colorless	216	45.34 (45.02)	7.71 (7.56)	8.26 (8.08)	20.17 (20.47)	18.35 (18.87)
$Zn(DPP)Br_2$	Colorless	209	36.16 (35.83)	6.18 (6.02)	6.61 (6.43)	36.30 (36.72)	14.70 (15.02)
$Zn(DPP)(NO_3)_2$	Colorless	220	38.67 (39.04)	6.76 (6.65)	14.27 (14.01)	30.86 (31.05)	16.06 (16.40)
$Cd(DPP)Cl_2$	Dirty white	237	39.96 (39.64)	6.80 (6.66)	7.39 (7.12)	18.37 (18.02)	28.29 (28.57)
$Cd(DPP)Br_2$	Colorless	230	32.61 (32.34)	5.62 (5.43)	5.92 (5.80)	32.93 (33.14)	23.05 (23.31)
$Cd(DPP)(NO_3)_2$	Colorless	180	35.05 (34.49)	5.71 (5.87)	12.76 (12.54)	27.13 (27.78)	25.37 (25.18)
$Hg(DPP)Cl_2$	Colorless	112	32.76 (32.39)	5.67 (5.44)	5.98 (5.81)	14.30 (14.73)	41.34 (41.66)
$Hg(DPP)Br_2$	Colorless	108	27.69 (27.34)	4.83 (4.59)	5.13 (4.91)	28.49 (28.02)	34.33 (35.17)
$Hg(DPP)(NO_3)_2$	Colorless	118	29.44 (29.17)	4.66 (4.60)	10.58 (10.47)	22.17 (23.18)	36.61 (37.50)
$Co(DPP)Cl_2$	Blue	168	46.17 (45.88)	7.88 (7.71)	8.41 (8.23)	20.60 (20.86)	17.50 (17.34)
$Co(DPP)Br_2$	Deep Blue	209	36.65 (36.37)	6.30 (6.11)	6.67 (6.53)	37.49 (37.28)	13.64 (13.74)
$Co(DPP)(NO_3)_2$	Green	162	39.47 (39.70)	6.56 (6.67)	14.52 (14.24)	31.71 (31.53)	14.71 (14.99)
$Ni(DPP)Cl_2$	Green	172	46.23 (45.91)	7.92 (7.71)	8.47 (8.24)	20.98 (20.87)	17.16 (17.16)
$Ni(DPP)Br_2$	Green	228	36.69 (36.39)	6.36 (6.11)	8.72 (6.53)	37.03 (37.29)	13.62 (13.70)
$Ni(DPP)(NO_3)_2$	Green	165	39.98 (39.70)	6.46 (6.67)	14.47 (14.25)	31.67 (31.58)	15.27 (14.99)
$Cu(DPP)Cl_2$	Dark Green	136	44.54 (45.26)	6.79 (7.60)	8.33 (8.13)	20.46 (20.59)	18.57 (18.44)
$Cu(DPP)Br_2$	Blue	128	36.27 (35.98)	6.21 (6.05)	6.63 (6.47)	36.66 (36.87)	14.38 (14.66)
$Cu(DPP)(NO_3)_2$	Greeen	204	39.06 (39.22)	6.46 (6.59)	14.39 (14.08)	31.38 (31.19)	16.13 (15.98)

metal ion. Thus, 1,3-Dipiperidinopropane behaves as bidentate ligand like substituted propylenediamine coordinating through nitrogen atoms. The far IR spectra of the complexes show multiple bands in the region 345-380 cm^{-1} and 225-320 cm^{-1}. The former bands are due to ν(M-X) vibrations and later bands are assigned to ν(M-N) stretching vibrations. All the bands observed are weak and broad [29]. In Table-2, are listed molar conductance and magnetic moment values for DPP complexes. The molar conductance values ranges from 3.36 - 9.27 mS mol^{-1}. This shows that the complexes of DPP are non-electrolytes in these solvents, which clearly indicates that anions are coordinated with the metal atoms.

The magnetic moments of Co(II) complexes are in the range 4.60 - 4.74 B.M, which is characteristic for the presence of three unpaired electrons. The higher value of magnetic moment

Table-2: Conductance/Magnetic and UV/Visible Spectral Data

Compound	Solvent	Molar Conductance (mS) mol^{-1}	μ_{eff} (BM)	ν(cm^{-1})
$Zn(DPP)Cl_2$	Acetone	4.17	-	-
$Zn(DPP)Br_2$	Acetone	4.80	-	-
$Zn(DPP)(NO_3)_2$	Acetone	5.97	-	-
$Cd(DPP)Cl_2$	Acetone	3.36	-	-
$Cd(DPP)Br_2$	Acetone	3.92	-	-
$Cd(DPP)(NO_3)_2$	Acetone	6.43	-	-
$Hg(DPP)Cl_2$	Acetone	6.77	-	-
$Hg(DPP)Br_2$	Acetone	7.65	-	-
$Hg(DPP)(NO_3)_2$	Acetone	8.89	-	-
$Co(DPP)Cl_2$	DMSO	9.14	4.63	17000, 16130, 15270
$Co(DPP)Br_2$	DMSO	8.29	4.60	18520, 15750, 14930
$Co(DPP)(NO_3)_2$	DMSO	8.81	4.74	18180, 15040
$Ni(DPP)Cl_2$	DMSO	7.12	3.52	24100, 15870
$Ni(DPP)Br_2$	DMSO	7.35	3.58	25900, 14490
$Ni(DPP)(NO_3)_2$	DMSO	8.23	3.74	27030, 16260
$Cu(DPP)Cl_2$	Nitromethane	9.27	1.73	18870, 14600, 13160
$Cu(DPP)Br_2$	Nitromethane	8.29	1.78	18520, 14810, 12740
$Cu(DPP)(NO_3)_2$	Nitromethane	8.83	1.83	21740, 14180

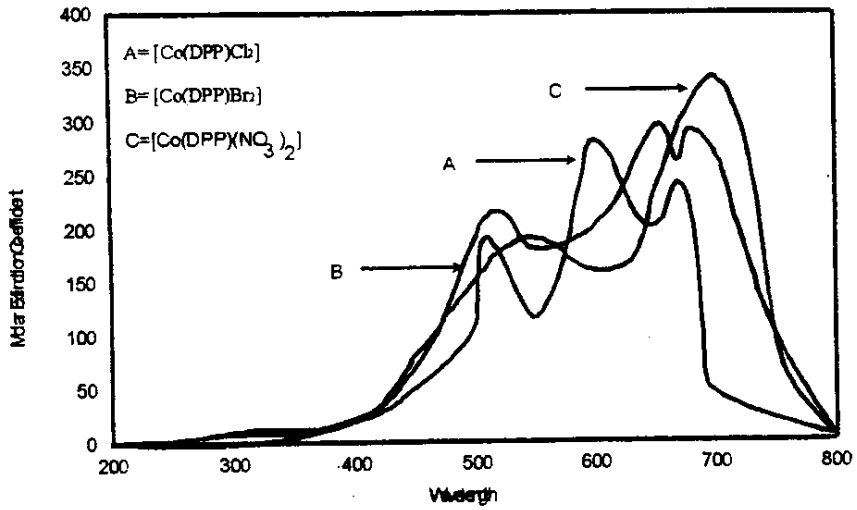

Fig. 1: Absorption spectra of DPP complexes in DMSO.

than the spin only moment is due to the orbital angular momentum contribution while that for Ni(II) complexes is 3.52 - 3.74 B.M, indicating the presence of two unpaired electrons. The magnetic moment of Cu(II) complexes lies in the range 1.73 - 1.83 B.M, characteristic for the presence of a single unpaired electron.

The $[Co(DPP)Cl_2]$ complex is blue, while $[Co(DPP)Br_2]$ is deep blue and $[Co(DPP)(NO_3)_2]$ is green. These complexes are non-electrolyte in DMSO. The solution spectra of the three complexes in DMSO are similar. The spectra is shown in Fig. 1 and data is presented in Table-2. The chloride complex exhibit three bands at 15270 cm^{-1}, 16130 cm^{-1} and 17700 cm^{-1}. Similar bands were observed for bromide complex with minor variations.

The absorption spectrum of nitrate complex is slightly different and only two bands at 18180 cm^{-1} and 15040 cm^{-1} were observed. These bands could be assigned to transition ν_3 in Td symmetry. The low energy transition ν_1 and ν_2 are not observed. The intensities and band positions are in accordance with Td symmetry [23].

The solution spectra of $[Ni(DPP)Cl_2]$, $[Ni(DPP)Br_2]$ and $[Ni(DPP)(NO_3)_2]$, complexes in DMSO are very much similar in band positions and intensities. The spectra are shown in Fig. 2 and data

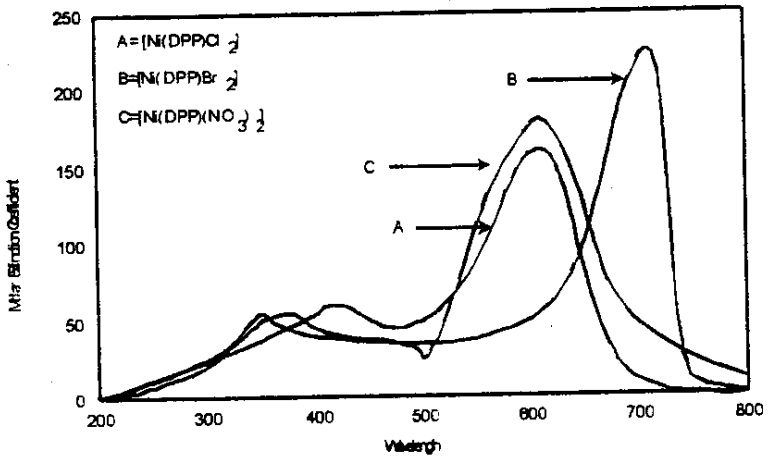

Fig. 2: Absorption spectra of DPP complexes in DMSO.

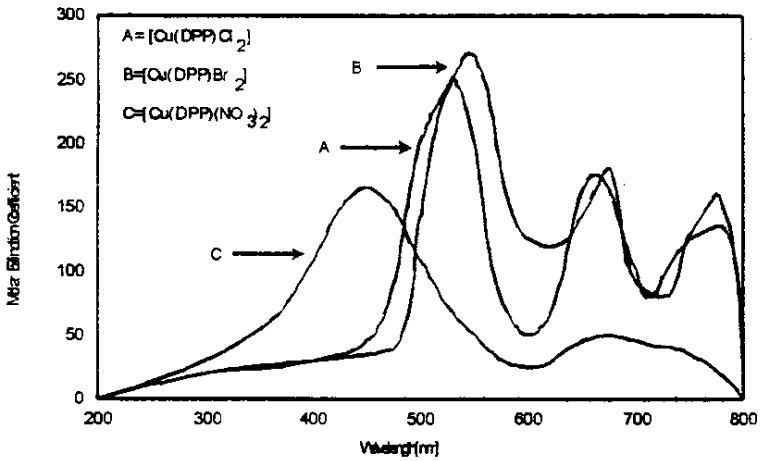

Fig. 3: Absorption spectra of DPP complexes in DMSO.

in Table-2. The non-electrolytic behaviour and the high spin type magnetic moments of 3.52 - 03.74 B.M. are indicative of Td geometry with nitrate ion as unidentate ligand. The strong bands observed at about 15500 cm^{-1} may be assigned to transition ν_3 and the band at about 25000 cm^{-1} [which has little higher value than the expected may be due to distortion in tetrahedral structure] to transition ν_1 in tetrahedral symmetry [24].

The solution spectra of chloride and bromide complexes of Copper(II) in DMSO are similar with some variation in band positions and intensities. The spectra are shown in Fig. 3 and data in Table-2. They clearly exhibit three absorption bands between 12000 to 22000 cm^{-1}, while only two bands were observed for nitrate complex. The complexes are non-electrolyte in nitromethane and have magnetic moments of 1.73 - 1.83 B.M. at room temperature. The electronic transitions observed in these complexes are consistent with C_{2v} symmetry.

In this symmetry four transition could be expected [25]. The fourth transition is not being observed as is the case in some previous investigations [26,27]. Similar spectra were observed for other Cu(II) complexes having CuN_2X_2 chromophore [23,28,29].

Experimental

Materials

Metal salts used were of reagent grade and used without further purification. The partial dehydration of the salt was done by drying the hydrated salts in vacuum oven for several hours at 80-100°C. All solvents were distilled at least once before using.

Table-3: Principal Infrared Bands (cm^{-1}) for DPP and its Metal Complexes.

Compound	ν(C-N)	ν(M-X)	ν(M-N)
DPP	1148s, 1117sh	-	-
$Zn(DPP)Cl_2$	1175m, 1160 sh, 1130w, 1112vs	375	295
$Zn(DPP)Br_2$	1178m, 1170sh, 1130m, 1115vs	370	290
$Zn(DPP)(NO_3)_2$	1178m, 1130sh, 1115vs	370	295
$Cd(DPP)Cl_2$	1175m, 1160sh, 1120sh, 1105vs	360	290
$Cd(DPP)Br_2$	1165m, 1150w, 1135w, 1105vs	350	280
$Cd(DPP)(NO_3)_2$	1170m, 1145w, 1115vs	365	280
$Hg(DPP)Cl_2$	1168m, 1155w, 1135sh, 1115vs	380	295
$Hg(DPP)Br_2$	1170m, 1155sh, 1130sh, 1120vs	380	285
$Hg(DPP)(NO_3)_2$	1168m, 1130sh, 1118s	370	290
$Co(DPP)Cl_2$	1165s, 1130vs, 1110s	355	300
$Co(DPP)Br_2$	1160vs, 1130vs, 1110s	350	295
$Co(DPP)(NO_3)_2$	1162s, 1150sh, 1135vs, 1108m	350	300
$Ni(DPP)Cl_2$	1160vs, 1130vs, 1105m	370	320
$Ni(DPP)Br_2$	1165vs, 1135vs, 1103m	365	225
$Ni(DPP)(NO_3)_2$	1165s, 1155sh, 1135s, 1108m	360	310
$Cu(DPP)Cl_2$	1160m, 1135sh, 1120vs	350	300
$Cu(DPP)Br_2$	1170w, 1160sh, 1130sh, 1118s	355	290
$Cu(DPP)(NO_3)_2$	1162s, 1138vs, 1115s	345	285

The ligands 1,3-dipiperidineopropane (DPP) was synthesized by the procedure already reported [32]. Piperdine (0.25 mole) in absolute methanol (40 ml) was added dropwise to (0.1 mole) dibromopropane in methanol (20 ml). The contents were refluxed for about 8 hrs at 80°C. The reaction mixture was left overnight to get piperidinium bromide crystals (m.p. 304°C) [32]. Yield was 80%.

Preparation of ligand solution

The ligand 1,3-Dipiperidinopropane (DPP) was dissolved in minimum amount of methanol, to

which a calculated amount of alcoholic potassium hydroxide was added and filtered to remove potassium bromide as precipitate. The filtrate was used as ligand solution.

Preparation solid complexes

All the complexes were prepared using similar general procedure. Approximately 10 m moles of partially dehydrated salt was dissolved in minimum amount of anhydrous solvent. Methanol was used as solvent for the preparation of $CoCl_2$, $CuBr_2$ and $NiCl_2$ complexes and ethanol for the synthesis of rest of the complexes. The ligand DPP, an excess over 1:2 metal to ligand ratio was also dissolved in minimum amount of the same solvent and slowly added to the hot metal salt solution with constant stirring. The mixture was stirred and kept at 50°C for half an hour, then cooled for about 20 minutes. The metal complexes precipitated either immediately or upon cooling. The product obtained was filtered through sintered glass crucible, washed several times with ether and dried under vacuum at 50°C. The complexes were recrystalized from acetone.

Instrumentation

Infrared spectra were taken in the range of 4000-600 cm^{-1} on PYE UNICAM infrared spectrophotometer as KBr disc. The far IR spectra were examined as KBr discs in the region 400-200 cm^{-1} (FT-IR Shimadzu).

The absorption spectra of solutions of complexes in the range 200-900nm using different solvents were obtained on Jasco DEC-1 spectrophotometer with 1 cm matched quartz-cells. Mass spectrum was recorded with MAT 312 mass spectrophotometer.

Molar conductance of the solution of metal complexes were carried out with a conductivity meter type H1 8333. All measurements were done at room temperature on freshly prepared solutions.

Magnetic susceptibilities were measured by Guoy method at room temperature using $Hg[Co(SCN)_4]$ as standard. The magnetic moments were calculated [33].

The elemental analyses were carried out at HEJ Research Institute of Chemistry, University of Karachi. The cations and anions were estimated by usual analytical procedure [34].

Conclusions

The stoichiometry of the complexes indicates that one DPP molecule coordinates with these metal ions. The conductance studies carried out in various solvents show that all the complexes are non-electrolytes and anions are coordinated with the metal ions. The IR spectra in solid phase clearly favors the formation of nitrogen coordination and thus support the bidentate behaviour of the ligand to form tetrahedral complexes of the type $[MLX_2]$. The magnetic moment studies and the solution electronic spectra further substantiate the tetrahedral coordination geometry around the central metal ion.

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