

The Structural Studies of Complexes of 1,3-di-(1*H*-imidazol-1-yl)-2-Propanol

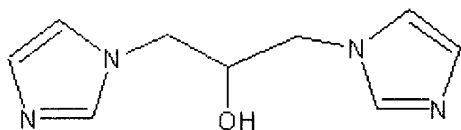
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Summary: The ligand 1,3-di (1*H*-imidazol-1-yl)-2-propanol (DIPO) is a modified form of Diimidazolopropane (DIP) whose complexes with copper (II) and cobalt (II) have been prepared. The characterization of ligand as well as that of complexes has been done through mass, conductance, magnetic moments, nmr, ir, and UV/visible measurements and elemental analysis. These measurements indicate that DIPO enforces tetrahedral structure to the complexes of cobalt (II) and copper (II). TGA and DTA have also been carried out.

Introduction

Much work has been done on the coordination chemistry of the complexes of acyclic/cyclic chelating agents containing grouping $>N-(CH_2)_n-N<$ in their structures. The representative ranges from ethylenediamine to diazacyclooctane etc [1, 2]. They enforce various geometries to the complexes from octahedral to tetrahedral/square planar. Various modifications to these chelating agents have been made and their complexes had been studied. The modifications in acyclic diamines are made by either replacing the terminal hydrogens with different electron donating moieties or by introducing additional methylene groups in between the terminal amine functions like dimorpholinoethne (DME) and dimorpholinopropane (DMP) [3-7]. 1-(*N*- β -ethyl-morpholine)-5-nitroimidazole (EMNI) is another modified form of such series, a chemotherapeutic reagent (naxogen or nitroimidazole) with high activity against *trichomonas vaginalis* and other *protozoa*, has been studied as a chelating agent [8]. The modifications of cyclic diamines were also reported in literature by replacing the hydrogens attached to the nitrogen with that of acetate group of diazacycloheptae (DACH) and diazacyclooctane (DACO) [9, 10].



1,3-di-(1*H*-imidazol-1-yl)-2-Propanol
(DIPO)

Keeping the same pattern in mind a new chelating agent 1,3-di-(1*H*-imidazol-1-yl)-2-propanol (DIPO) a derivative of imidazole[11-12] (widely distributed in nature as histidine moiety) has been prepared in accordance with Gero's method [11].

The above ligand can be viewed as modified form of DMP, as the morpholino moiety has been replaced with imidazole. To this chelating agent OH group has been attached to the central carbon of propane in order to study its influence on its coordination properties. Imidazole is an excellent donor towards metal ions and form stable complexes. Some of its derivatives have very interesting and useful properties. In fact the 2-methyl imidazole is used as an herbicide [14]. Another derivative 2-hydroxybenzene-benzimidazole has antiviral activities [15]. The coordination chemistry of imidazole and its derivatives is quite interesting and well documented [16].

The complexes of (DIPO) ligand have been prepared and their structures are elucidated on the physical measurements such as conductance and magnetic moments along with IR, ¹H-NMR, mass, UV/Visible. The thermal stabilities have been also checked through TGA and DTA.

Results and Discussion

The ligand is characterized by melting point, elemental analyses, mass, NMR and IR spectra. The complexes are characterized by their elemental

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analyses, where as the structural assignments are made on conductance measurements, magnetic susceptibility, IR and UV-visible spectra. In addition to characterization of complexes the thermal measurements are also studied. Proton NMR-spectrum of 1,3-*di*-(1*H*-imidazol-1-yl)-2-propanol (DIPO) in DMSO- d_6 with TMS as internal standard is shown in. ^1H NMR spectrum given in Fig. 1 and assignments are on the structure.

The ligand is further confirmed by the mass spectra also (Fig. 2). A mass peak of moderate intensity was observed at m/z 192 which corresponds

to molecular ion $(\text{C}_9\text{N}_4\text{H}_{12}\text{O})^+$. A base peak at m/z 81 is due to N-methyl imidazole $(\text{C}_4\text{N}_2\text{H}_5)^+$, while the signal at m/z 111 could be assigned to hydroxy ethyl imidazole $(\text{C}_4\text{N}_2\text{H}_7\text{O})^+$.

The ligand 1,3-*di*-(1*H*-imidazol-1-yl)-2-propanol behaves as bidentate ligand and bears resemblance to 1, 2-dimorpholinoethane, 1, 2-dipiperidino propane. The elemental analysis data in Table 1 indicates that only one DIPO molecule like that of DME and DPE is coordinated with metal ion to form complexes of general formula $[\text{M}(\text{DIPO})\text{X}_2]$ where $\text{M} = \text{Co}(\text{II}), \text{Cu}(\text{II})$ and $\text{X} = \text{Cl}^-, \text{Br}^-$.

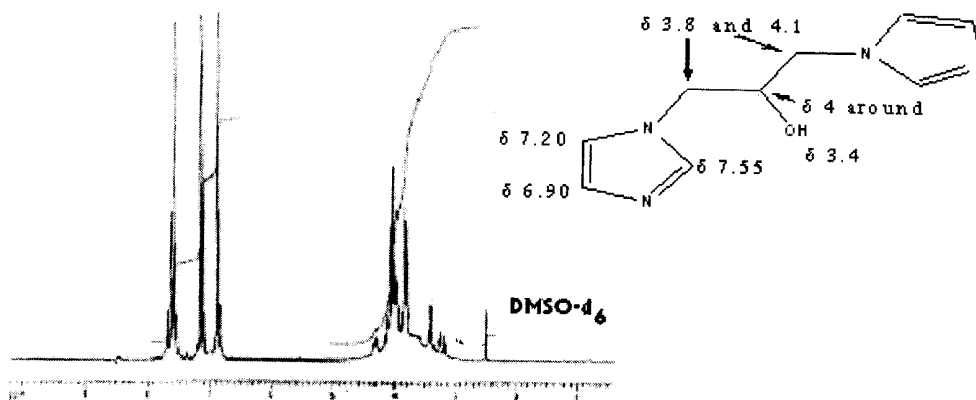


Fig. 1: ^1H -NMR spectra of DIPO.

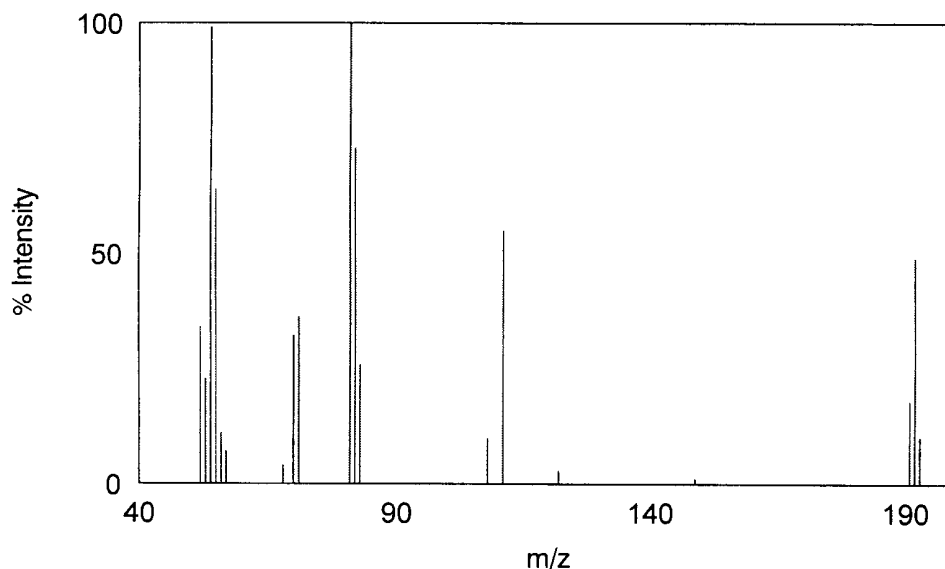


Fig. 2: Mass spectra of DIPO.

Table-1: Analytical data for DIPO and its complexes.

Compound	Mt.pt °C	Colour	%C		%H		%N		%METALS		%ANIONS	
			Calc	Found	Calc	Found	Calc	Found	Calc	Found	Calc	Found
DIPO	192	Colour less	56.24	56.09	6.29	6.15	29.15	28.79				
[Co(DIPO)Cl ₂]	91	Blue	33.56	33.47	3.76	3.54	17.40	17.29	18.30	18.09	22.02	21.90
[Cu(DIPO)Cl ₂]	95	Blueish green	33.09	32.86	3.70	3.52	17.15	17.07	19.45	19.31	21.71	21.68
[Cu(DIPO)Br ₂]	87	Brown	26.01	25.83	2.91	2.43	13.48	13.32	15.29	15.09	33.45	33.01

The molar conductance values are given in Table-2 ranging from 1.2 to 4.8 m.s. mol⁻¹. These values indicate that the complexes are non electrolytic in nature. The magnetic moment of Co (II) complex has 4.37 B.M which is characteristic value for the presence of three unpaired electrons. While that for Cu (II) complexes it is 2.0 and 2.2 BM [17].

Table-2: Conductance and magnetic moments.

Complexes	Solvent	Molar conductance $\mu(m s mol^{-1})$	μ_{eff} (BM)
[Cu(DIPO)Br ₂]	DMSO	4.8	2.2
[Cu(DIPO)Cl ₂]	DMSO	3.7	2.0
[Co(DIPO)Cl ₂]	DMSO	1.2	4.3

The characteristic bands in the infrared spectra (4000-600 cm⁻¹) of DIPO and its metal complexes are given in (Table 3). The infrared spectrum of the free ligand, DIPO in KBr exhibits a strong absorption bands at 1511 cm⁻¹ and a weak band at 1592cm⁻¹. These bands are assigned to C=N stretching vibrations. The ligand also exhibits a strong absorption band at 1107 cm⁻¹ and a weak band at 1080 cm⁻¹. These bands are assigned to C-N stretching vibrations. Ligand also shows a broad peak at 3219 cm⁻¹ which is assigned to -OH. In Cu (II) chloride complex the band at 1511 cm⁻¹ is shifted to lower frequency at 1506 cm⁻¹ whereas the band 1592 cm⁻¹ shifts towards higher frequency at 1558 cm⁻¹. Similarly bands due to C-N stretching vibrations, the strong one move to lower frequency side and is observed at 1010 cm⁻¹ the other weaker band is observed at 1166 cm⁻¹. Similar results were recorded for [Cu (DIPO) Br₂] and [Co (DIPO) Cl₂].

Table-3: IR data of DIPO and its complexes.

Compound	Stretching $\nu(C-N) cm^{-1}$	Stretching $\nu(C=N) cm^{-1}$	Stretching (-OH) cm ⁻¹
Ligand	1080s, 1107sh	1511vs, 1592s	3219
[Cu(DIPO)Br ₂]	1031vs,	1521s, 1558w	3210
[Cu(DIPO)Cl ₂]	1010w, 1160s	1506s, 1521sh	3211
[Co(DIPO)Cl ₂]	1095s, 1166w	1508s, 1521vs, 1558s	3210

The visible spectra of chloride and bromide complexes of Cu (II) in DMSO are similar with minor variations in band positions and intensities.

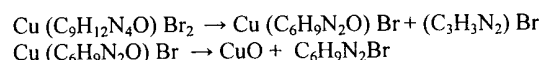
The electronic transitions observed in these complexes are consistent with C_{2v} symmetry. In this symmetry four transitions could be expected [18]. The fourth transition is not being observed in accordance with the previous investigations [18-19]. They resemble Cu (II) complexes having CuN₂X₂ chromophoric environment [20]. All these various data leads to the tetrahedral structure of the complexes.

Table-4: Visible Absorption data of DIPO.

Compound	Wavelength (nm)	Energy (cm ⁻¹)	Assignment
[Cu(DIPO)Br ₂]	822	21165	d-d transition
[Cu(DIPO)Cl ₂]	832	12019	d-d transition
[Co(DIPO)Cl ₂]	633	15785	⁴ A ₂ (F) → ⁴ T ₁ (P)
	610	16393	⁴ A ₂ (F) → ⁴ T ₁ (P)
	582	17182	⁴ A ₂ (F) → ⁴ T ₁ (P)

The solution spectra of Co (II) complexes in DMSO exhibit three absorption bands at 17182 cm⁻¹, 16393 cm⁻¹ and 15785 cm⁻¹ (Fig 3). These bands could be assigned to transition ⁴A₂(F) → ⁴T₁(P), v₃ in T_d-symmetry.

The TG and DTA curve for the complex of Cu(C₉H₁₂N₄O)Br₂ is shown in fig 4. The thermal degradation of this complex is summarized below in the form of equation.



The thermal degradation of the rest of the complexes is given in table 5. The detailed thermal degradation will be reported in near future as an independent communication.

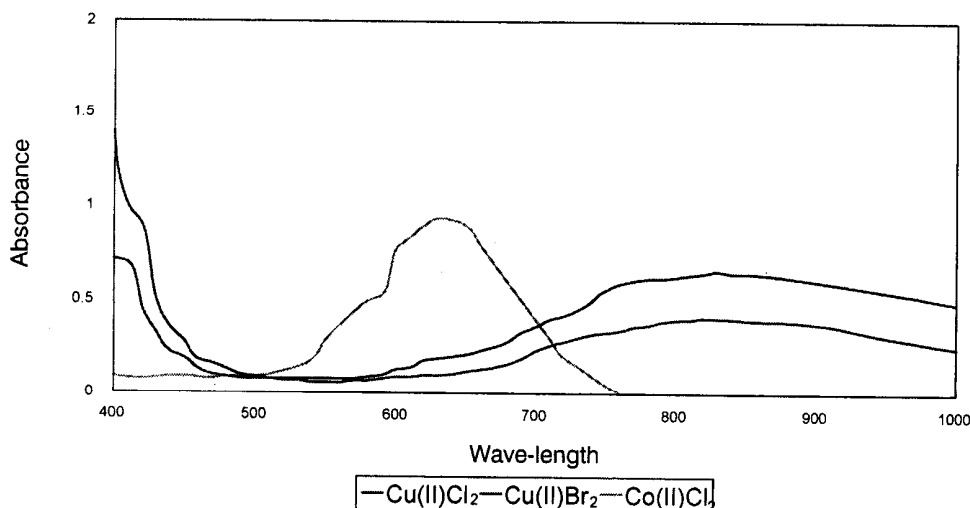
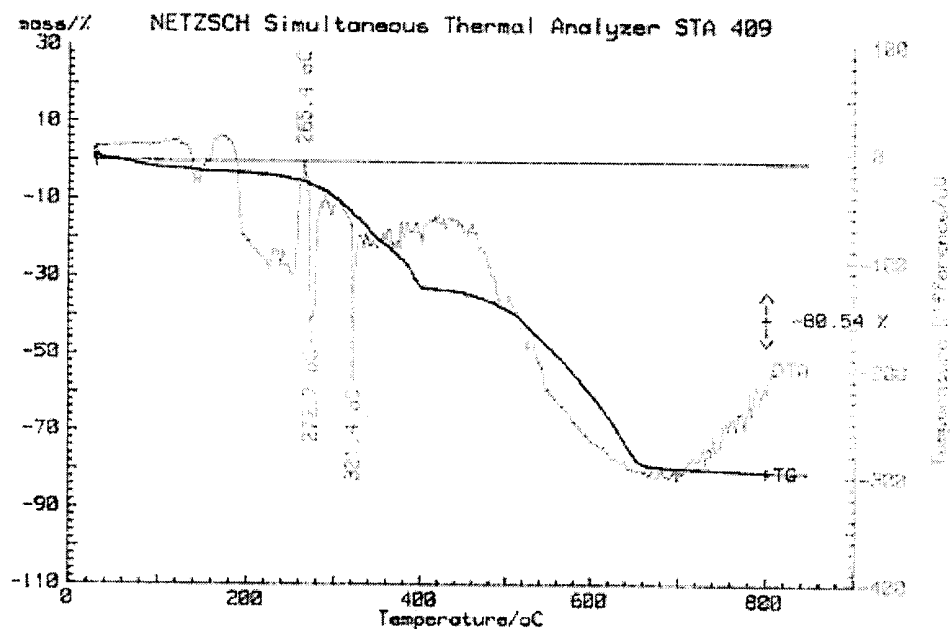
Experimental

Ligand Preparation

To 0.02 moles (1.36 g) of imidazole in 50 mL ethanol was added 0.02 moles (1.12g) of potassium hydroxide in small portion with constant stirring over a period of half an hour at room temperature. To the resultant mixture 0.01 mole (0.9g)

Table-5: Thermal data of DIPO and its complexes.

Compound	Temp. °C	Weight loss %		Decomposition product	DTA curve
		Calc	Found		
[Cu (DIPO) Cl ₂]2H ₂ O	0-100	9.93	10.00	2H ₂ O	
	100-440	22.62	21.00	C ₃ H ₂ N ₂ O ₂	endo 263°C 299°C
	440-800	30.38	31.74	C ₆ H ₉ N ₂	endo 469°C 487°C exo 523°C
[Cu (DIPO) Br ₂]4H ₂ O	100-380	37.07	37.06	CuCl ₂	
		31.99	32.00	C ₃ H ₁₃ N ₂ O ₅	exo 265°C, endo 272°C, 321°C
	420-800	55.36	48.54	C ₆ H ₉ N ₂ Br ₂	
[Co (DIPO) Cl ₂]6H ₂ O	200-400	20.00	16.31	CuO	
	200-400	29.08	29.00	C ₄ H ₂ N ₂	exo 204°C, 373°C
	460-600	40.73	40.39	C ₃ H ₁₀ N ₂ O	endo 529°C
		30.18	30.61	CoCl ₂	

Fig. 3: Visible spectra of complexes CuCl₂, CuBr₂, CoCl₂ with DIPO.Fig. 4: Thermogram of [Cu (DIPO) Br₂].

of epichlorohydrin was added and the stirring was continued for another 4 hours. KCl was settled down and then filtered. Ethanol was removed through rotary evaporator. Yield of this product was 91%.

Preparation of Complexes

All complexes were prepared by the same general procedure. A calculated amount of partially-dehydrated salt was dissolved in minimum amount of solvent (ethanol). The solution was stirred for 1 hour at room temperature. Ligand to metal ratio 1:1 was used. Complexes were precipitated and washed with ethanol several times. They were recrystallized before measuring various properties

Instrumentation

Physical Measurements

The elemental analysis of the complexes and ligand were performed through the courtesy of HEJ Research Institute of Chemistry, University of Karachi. The metal ion and anions were analyzed through INCA 200 EDS (Oxford). The Infrared spectra of the ligand and solid complexes were recorded on KBr disc with model 270-50 Hitachi Infrared spectrophotometer. The ¹H-NMR spectrum in DMSO for ligand was obtained with Bruker (AM 400) using TMS as an internal standard. A mass spectrum of ligand was recorded with MAT-312 mass spectrophotometer. Conductance measurements were made with AGB 1000 England. Magnetic susceptibilities were measured by the Gouy method at room temperature using the Hg[Co(NCS)₄] as the standard. TGA and DTA were carried out through the courtesy PINSTECH, Islamabad.

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