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Studies on metal (II) complexes of bisazo dye 2, 2¹ [benzene-1,3-diyl di (E) diazene 2,1-diyl] dianiline

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ABSTRACT

Co (*II*), *Cu* (*II*), *Mn* (*II*), *Ni* (*II*) and *Zn* (*II*) complexes of a novel bisazo dye 2, 2¹ [benzene-1, 3-diyl di (*E*) diazene 2, 1-diyl] dianiline were synthesized. Characterization of the ligand and metal complexes has been done on the basis of elemental analysis, mass, FT-IR, ¹H NMR, magnetic data and thermal analysis (TGA). From the analytical and thermal data, the stoichiometric ratio of the complexes has been found to be 1:1(metal-ligand). On the basis of physic-chemical data octahedral and square planar geometries were assigned for the azo complexes.

Keywords: bisazo, thermal, magnetic

INTRODUCTION

Azo compounds are very important molecules and have attracted much attention in both academics and applied research. Thermal properties and suitable absorption band of azo compounds are essential features in relation to their application as high-density optical recording molecules. Besides their classical applications in synthetic dyes and pigments, azo compounds find increasing accessibility in photo responsive biomaterials and supramolecular system. On the other hand, metal-complex dyes find application as powerful charge-control agents (CCAs) for toners to create a desired charge level and polarity [1-4].

MATERIALS AND METHODS

All the chemicals and solvents used were of analytical grade. Metal (II) salts were used as acetates. The electronic spectra were recorded on a Shimadzu UV-Visible 1650 PC spectrophotometer in the wavelength range of 200-600 nm using 1cm matched quartz cells. Infrared spectra of ligand and complexes were recorded in the region of 4000 cm⁻¹ - 400 cm⁻¹ on a FT-IR 8400s SHIMADZU spectrometer using KBr pellets. The ¹H NMR spectra were recorded in DMSO-d₆ at 400 MHz using amx400 FT-NMR spectrometer. Elemental analyses of C, H and N were done on a Vario EL III CHN elemental analyser. Mass spectrum of the ligand was recorded with a LC-MSD-trap-XCT plus mass spectrometer. The molecular melting points were determined by open capillary method using electric melting point apparatus. The magnetic susceptibilities at room temperature were measured by Gouy method.

Synthesis of ligand and complexes

Meta phenylenediamine (1.08g / 0.01mol) was dissolved in a mixture of $5cm^3 of$ water and $10cm^3$ of concentrated hydrochloric acid, while 20 ml of concentrated hydrochloric acid was diluted with crushed ice. To this a cold

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solution of sodium nitrite (2.5g/10 ml water, 0.036mol) was added over a period of 30 minutes with continuous stirring. Immediately m-phenylenediamine hydrochloride solution was added and stirred for about 1hr till a dark yellow colored solution was obtained [8]. The coupling agent aniline dissolved in glacial acetic acid (0.02mol) was cooled and added to the tetrazo solution slowly with continuous stirring and maintaining the temperature 0-5°C. The resulting solution was stirred well and sodium acetate solution (7g/50ml water) was added till neutralization. The dye was washed with cold water and collected by vacuum filtration and purified by several recrystallizations from water and alcohol.

A solution of 4mmol of metal acetate in 10ml methanol was added to methanol-chloroform (1:1v/v) solution containing 8mmol of ligand and was refluxed for 2hrs. The obtained solution was left at room temperature. The precipitated complex was filtered, washed with methanol and then recrystallized from methanol-chloroform (1:3v/v) and dried in vacuum. The yields of all the complexes were almost quantitative.

RESULTS AND DISCUSSION

Characterization of compounds

All the synthesized compounds were intensely colored amorphous solids. The ligand was reddish brown solid, Melting point: $88-90^{\circ}$ C and yield 82 %, soluble in DMSO while the metal complexes were sparingly soluble in DMF and DMSO. The data were summarized in table1.

MW: 316, MS: m/z 316 (RI=100%), m/z 214 (RI=20%), [M-NC₆H₄NH₂], m/z 198 (RI=28%) [M-NC₆H₄NH₂]. The signal appeared in the mass spectrum (Fig 1) confirms the proposed formula. The signal at m/z 214 is due to the cleavage of one of the N=N bond and the fragment ion at m/z 198 is due to the product of the cleavage of C-N bond. ¹H NMR (253.13MHz)/DMSO-d⁶/ δ (ppm): 6.58-8.28 (12H, aromatic), 1.90 (4H, NH₂), 2.49& 3.49 (DMSO protons). (Fig 2).





Fig 2. NMR spectra of ligand FTIR analysis

IR absorption spectra of all the synthesized compounds were recorded in the wave length range of 400-4000cm⁻¹. The IR data of the azo dyes and their metal complexes were presented in Table 1. The IR spectra of complexes were compared with that of the free ligand in order to determine the co-ordination sites involved in chelation. There were

some guide peaks in the spectra of ligand, the position of these peaks were expected to change upon chelation. More common sharp peaks were observed in dye and complexes in the region of 1625-1400 cm⁻¹ which were assigned to - N=N- stretching vibration. Upon comparison, it was found that the (N=N) stretching vibration in free ligand gets shifted in complexes, indicating the participation of azo nitrogen in co-ordination with the metal (M-N). Aromatic N-H stretching vibrations were assigned in the range of 3500-3250 cm⁻¹. New bands found in the spectra of all the complexes in the region 420-500 cm⁻¹ have been assigned to metal-ligand vibrational frequencies [5-10].



Fig 4. IR absorption spectra of Co (II) complex

SI No.	Mol. Formula		Elemental analysis Calculated Found		IR absorption bands	
	Mol. weight	Proposed structures				
01	PdBaAn C ₁₈ H ₁₆ N ₆ 316.35		C:68.34 H:5.10 N:26.56	C:67.84 H:4.91 N:27.25	1623, 3392, 2852, 1392, 1336.	
02	Co-PdBaAn C ₁₈ H ₁₄ N ₆ Co 373.27	HN N N N N N	C:57.92 H:3.78 N:22.51 Co:15.79	C:56.35 H:4.39 N:23.25 Co:16.01	1650, 3580, 1573, 1371. 451, 838.	
03	Cu-PdBaAn C ₁₈ H ₁₄ N ₆ Cu 377.89	HN N N N N N N N	C:57.21 H:3.73, N:22.24 Cu:16.82	C:58.17 H:3.31 N:21.68 Cu:16.84	1649, 3581, 1546, 1377. 459, 840.	
04	Mn-PdBaAn C ₁₈ H ₁₄ N ₆ Mn 369.28	HN NN NN NN NN	C:58.54 H:3.82 N:22.76 Mn:14.88	C:57.54 H:4.13 N:22.79 Mn:14.91	1598, 3641, 1542, 1390. 449, 837.	
05	Ni-PdBaAn C ₁₈ H ₁₄ N ₆ Ni 373.03	HN Ni NN NN	C:57.95 H:3.78 N:22.53 Ni:15.73	C:58.26 H:3.22 N:23.05 Ni:15.47	1600, 3469, 1485, 1367. 441, 838.	
06	Zn-PdBaAn C ₁₈ H ₁₄ N ₆ Zn 379.75	HN Zn N	C:56.93 H:3.72 N:22.10 Zn:17.22	C:57.72 H:4.13 N:21.07 Zn:17.08	1639, 3463, 1558, 1388. 445, 840.	

Table 1: Proposed structure, elemental analysis and IR data of synthesized compounds

Electronic spectral studies

The electronic spectral studies of all the synthesized ligands and their metal complexes have been carried out in dimethyl sulfoxide. The formation of metal (II) azo complexes was also confirmed by their UV-VIS spectra. While the λ_{max} of complexes were slightly red shifted which arise from the energy change of intense π - π * and n-

 π^* transition of the conjugated chromophore due to the chelation between metal ions and azo ligand. The complexation of the dye with the metal ion was responsible for a significant hypochromic shift at both π - π^* and n- π^* transition region [12-17]. The electronic absorption data were depicted in Table 2 and spectra were shown in Figure 3.

compounds	DMSO			
	$\lambda_{max}(nm)$	absorbance		
Azo ligand	276	3.51		
	398	4.12		
Co^{2+}	278	3.70		
	407	4.12		
Cu ²⁺	280	4.23		
	390	4.18		
	414	4.20		
Mn ²⁺	279	3.75		
	392	4.16		
	407	4.16		
Ni ²⁺	282	4.06		
	399	4.21		
	433	4.24		
Zn^{2+}	270	3.80		
	399	4.20		
	420	4.21		

Table 2. Absorption data of ligand and complexes



Fig 5. Electronic spectra of dye and complexes

Thermal studies

TGA curves were recorded for metal complexes of azo dyes in the range of 25 - 600 ^oC in air at the heating rate of 10^{0} C/min. The thermodynamic activation parameters of decomposition of dehydrated complexes, namely activation energy (E*), enthalpy (Δ H*), entropy (Δ S*) and Gibbs free energy change of decomposition (Δ G*) were evaluated graphically by using Broido's method [18-21].

The thermal stability data were listed in Table 3. The data clearly indicated that the decomposition of the complexes proceeds in single step. Water molecules were lost between 50° C and 200° C and metal oxides were formed above 500° C. The decomposition was complete at > 500° C for all complexes. The degradation pathway for all complexes may be represented as

 $[ML (H_2O)]_n H_2O \rightarrow [ML (H_2O)] + nH_2O$

$[ML (H_2O)] \rightarrow H_2O + [MO \text{ or } MO_2]$ Where MO= CuO, CoO, NiO, ZnO and MO₂= MnO₂.

The major weight loss for all the complexes was found in the range of $185-568^{\circ}$ C. The observed thermal stability was in the order Ni > Co > Cu > Zn >Mn. Thermodynamic data reveals that Ni complex has the highest activation energy of 11.14 kJ/mole. It was clear from the TGA of complexes that high activation energy causes rapid degradation around their decomposition temperatures, whereas low activation energies represent gradual degradation. The entropy of activation had negative values for all the complexes, which indicate that the decomposition reactions proceed with a lower rate than the normal ones.

Compound	Decomposition Temperature	Activation energy E* kJ/mole	Frequency factor $\ln A$, min ⁻¹	∆ H* kJ/mole	Δ S* J/K	ΔG^* kJ/mole
	(°C)					
Co-PdBaAn	292-516	5.06	8.40	5.62	-160.34	108.63
Cu- PdBaAn	238-472	4.24	8.54	5.22	-157.02	98.68
Mn-PdBaAn	185-529	6.02	8.24	5.23	-162.35	102.27
Ni- PdBaAn	305-495	11.14	7.01	5.58	-198.34	133.47
Zn- PdBaAn	191-568	6.58	8.13	5.00	-162.44	97.87



Fig 6. TGA thermograms

Fig 7. plot of ln(ln1/y) vs 1/T for complexes of PdBaAn

Magnetic susceptibility measurements

The magnetic moment values for cobalt complexes were ranging from 4.03-5.01 B.M. which were in fair agreement with the predicted values of octahedral geometry.

The magnetic moment values for copper (II) chelates ranging from 1.78-2.01 B.M. which were close to the spin only value for a tetrahedral or square planar geometry. The slightly higher of the magnetic moment of the Cu^{2+} also supports the same.

The magnetic moments of Mn (II) complexes were calculated from the magnetic susceptibility measurements and were found to be in the range of 5.48-5.88 B.M., indicating the presence of five unpaired electrons and hence were high spin complexes.

All the Ni (II) complexes were found to be paramagnetic. The magnetic moment values for these complexes ranging between 3.09-3.66 B.M. which were in good agreement with the predicted values of octahedral geometry. The Zn (II) complexes were diamagnetic in nature since Zn^{2+} is having a d¹⁰ system as expected.

CONCLUSION

The synthesized azo metal (II) complexes have potential application for high density optical recording media due to their absorption spectra and high thermal stability. Further work with analogs is needed.

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