Synthesis and Characterization of New Azo Ligand and Its Co(II), Cu(II), Zn(II) and Ni(II) Complexes

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This study describe the synthesis and characterization of new azo ligand, 5-hydroxy-4-(2,4-dihydroxyphenylazo)-2,7-naphthalene disulfonic acid disodium salt (L). The Cu(II), Zn(II), Ni(II) and Co(II) complexes of the azo ligand were prepared and characterized by infrared, UV-visible, ^{1}H and ^{13}C NMR spectra, atomic absorption spectroscopy, mass spectrometry, elemental analyses, thermogravimetric analysis, conductivity and magnetic measurements. The results suggest that the complexes have a 1:1 (metal:ligand) molar ratio, involving mononuclear azo ligand with an ONO donor set. Metal ion uptake studies were conducted with a batch technique. The results indicate that the azo ligand has high thermal stability and good metal extraction capacity.

Keywords: Azo ligand, Metal complexes, Metal ion uptake, Thermal stability.

INTRODUCTION

Because of the good thermal stability of azo compounds, one of the most important applications of azo compounds is in the optical data storage[1]. In general, cyanine dyes, phthalocyanine dyes and metal-azo complex dyes are used for DVD-R (digital versatile disc-recordable) as recording layer. Based upon the consideration of the above requirements, the thermal properties of azo compounds play an important role in application of azo dyes and their azo-metal complexes dyes. These compounds form an important class of colorants which consist of at least a conjugated azo (-N=N-) chromospheres[2]. These interactions have created the great interest amongst chemists and led to the study of azo dyes as analytical reagents, histological stains, antimicrobial activity and ink-jet printer dyes[3-6]. H-acid azo derivatives (H-resorcinol, beryllon III) are known as reagents for the photometric determination of boron, beryllium and some other elements[7,8]. However, the thermal stability and metal ion uptake capacity of these compounds has not been adequately studied. In this study, we reported our investigations in to the synthesis and characterization of new azo ligand and its metal complexes (Fig. 1).

EXPERIMENTAL

1,3-Dihydroxybenzene, 4-amino-5-hydroxy-2,7-naphthalene disulfonic acid monosodium salt, CuCl$_2$·2H$_2$O, CoCl$_2$·6H$_2$O, NiCl$_2$·6H$_2$O, ZnSO$_4$·7H$_2$O, HCl, EDTA and sodium nitrite were obtained from Merck (reagent grade). All of the used solvents were used solvent grade. 4-Amino-5-hydroxy-2,7-naphthalene-

disulfonic acid monosodium salt was recrystallized from ethanol/water (1:1), followed by the addition of HCl to pH 3. Doubly distilled water was used for the preparation of all solutions, titrations and metal ion uptake studies. Standard stock solutions were prepared by dissolving an appropriate molar amount of Cu(II), Co(II), Zn(II) and Ni(II) salts in ethanol. After acidic decomposition of the complexes, the levels of metal ion content were determined by potentiometric titrations and atomic absorption spectroscopy. IR spectra (4000-400 cm^{-1}) were obtained as KBr pellets on a Perkin-Elmer RXI FT-IR system spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400-200 NMR spectrometer, with all samples dissolved in DMSO-d_6 using tetramethylsilane as internal standard. EA (C, N and H) were performed using a CHNS-932 (Leco) elemental analyzer. All percentages of the metal ions of the complexes were determined using an Ati-Unicam model-929 atomic absorption spectrophotometer. UV-visible spectra were recorded using a TU-1901 PC spectrophotometer. All electronic spectra were measured in distilled water. The mass spectra were recorded on a Micromass UK Platform-II. Magnetic measurements were carried out at 25 °C using a Sherwood Scientific magnetic susceptibility balance with CuSO$_4$·5H$_2$O as standard. Magnetic susceptibilities were calculated as the Bohr Magneton using the $\mu_{eff} = 2.83 \sqrt{X_m.T}$ equation. TGA was performed on a Shimadzu DTA 50 model using 10 mg samples. Molar conductivities were determined in water (10^{-3} M) at 25 °C using a Tacussion model conductivity meter. Melting points were determined by a Gallenkap model

melting point apparatus. Potentiometric titrations and pH adjustments were carried out on a Selecta instrument equipped with a combined glass calomel electrode.

Synthesis of azo ligand: Azo ligand was synthesized according to the literature[9]. 4-Amino-5-hydroxy-2,7-naphthalene-disulfonic acid monosodium salt (10 mmol, 3.40 g) was mixed with HCl (37 %, 1 mL, 13.4 mmol) in ice particles (20 g) and diazotized below 5 °C with sodium nitrite (11 mmol, 0.75 g) in distilled water (20 mL). The resulting compound was coupled to the 1,3-dihydroxybenzene, (10 mmol, 1.11 g) in alkaline media below 5 °C. The pH was kept between 8 and 10 during the course of the coupling reaction. Coupling to the 1,3-dihydroxybenzene took place in basic media at the position *ortho* to the hydroxyl group (Fig. 1)[11]. Upon completion of the addition, the reaction was maintained in the ice bath for 0.5 h. Organic impurities were then extracted by washing with 20 mL of diethyl ether. The precipitated azo ligand was collected by filtration and dried under vacuum at 75 °C. Obtained azo ligand was recrystallized twice from ethanol/water (1:1), followed by the addition of HCl to pH 3. The purity of the azo ligand was evaluated by thin layer chromatography (TLC).
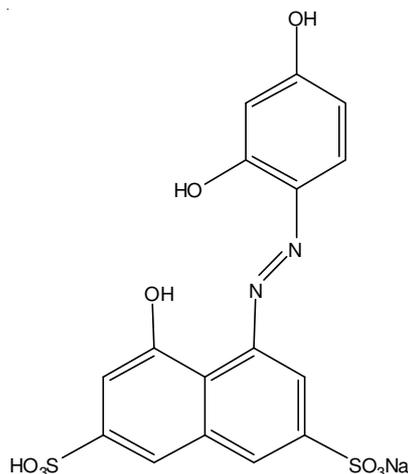

Fig. 1. Proposed structure of the ligand

Synthesis of the metal complexes: The metal complexes were synthesized by addition of the appropriate metal salt (1 mmol, in 25 mL absolute ethanol) to a hot solution of the azo ligand (1 mmol) in 30 mL distilled water. The pH was adjusted to 5 using alcoholic ammonia (0.01 M). The resulting solutions were stirred and heated on a water bath at 70 °C for 3 h. The volume of the obtained solution was reduced by half through evaporation. Cool ethanol was added to the solution and the resulting crystals were collected by filtration and washed with 25 mL mixture of ethanol and diethyl ether. The product was then dried under vacuum at 60 °C. The synthesized metal complexes were recrystallized from ethanol/water (2:1). The purity of all complexes was evaluated by TLC. All the complexes were isolated as solid powders.

Metal ion uptake studies: The metal ion uptake studies were done by a batch technique and the corresponding data are given in Table-3. The synthesized azo ligand has two sulfonate groups that assist in aqueous solubility. The addition of a barium nitrate solution (0.1 M, pH = 7) resulted in the precipitation of the insoluble barium salts of the azo ligand, which

was isolated by filtration and dried *in vacuo*. The precipitated azo ligand was used for all metal ion uptake studies. In the batch technique, a suspension of the azo ligand in a solution of metal salt of known volume and concentration was stirred magnetically for 6 h at 25 °C. The pH of solutions were adjusted using for standard buffers (pH = 4, 7 and 9). The precipitated azo ligand was powdered, sieved (100 mesh, ASTM) and suspended in water at pH = 5 for one day. The azo ligand was then filtered and washed two times with distilled water. The metal ion concentration in the filtrate and in the resulting washings was determined by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

The new tridentate azo ligand interacts with metal ions to form mononuclear, metal complexes with a proposed structure shown in Fig. 2. The Cu(II), Zn(II), Co(II) and Ni(II) chloride salts and azo ligand were reacted to yield complexes corresponding to the general formula $[ML·H_2O]·xH_2O$ (x = 2,3 and 4). The conductivities of solutions of the complexes in aqueous media (at 10^{-3} M) are shown in Table-1. All complexes were determined to be non-electrolytes, as their conductivity values ranged between 28 and 36 $ohm^{-1} cm^2 mol^{-1}$. The azo ligand and its complexes are soluble in DMSO, ethanol, DMF and water, but insoluble in other common organic solvents. Based on the magnetic, spectroscopic and elemental analysis, it is concluded that the metal ligand ratio of all the complexes was 1:1, with one water molecule per complex. Generally, *ortho*-functionalized azo ligands act as tridentate ligand in metal complexes[10]. The synthesized azo ligand is coordinated to the metal ions in a tridentate manner *via* the NOO atoms for each metal ion. The remaining coordination sites are occupied by water molecules. The metal content of the complexes was determined using atomic absorption spectroscopy. The decomposition points, yields, analytical and magnetic moment data of the complexes are also provided in Table-1.
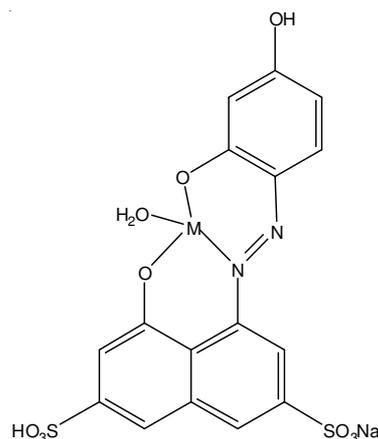
Fig. 2. Proposed structure of the metal complexes

Electronic spectra: The electronic spectra of the azo ligand and its metal complexes were measured in water (5. 10^{-5} M) at 25 °C. The spectroscopic maxima and molar extinction coefficients are reported in Table-2. The azo ligand and its metal complexes exhibited dye character since the molar extinction coefficients (e) were over 40 000 $M^{-1} cm^{-1}$ (maximum absorbance 0.50)[11]. The strong absorption at 230 nm was

TABLE-1
SOME ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE AZO LIGAND AND ITS COMPLEXES

Compounds	Empirical formula	m.w.	d.p. (°C)[a]	Yield %	μ_{eff} (BM)[b]	Found (Calcd.) %				Λ_M[c]
						C	H	N	Metal	
Azo Ligand	$C_{16}H_{11}N_2O_9S_2Na$	462.4	352	62	-	41.82 (41.56)	2.49 (2.40)	6.38 (6.06)	-	28
$[CuL\cdot H_2O]\cdot 2H_2O$	$C_{16}H_{15}N_2O_{12}S_2NaCu$	577.9	416	66	1.74	33.61 (33.25)	2.75 (2.62)	4.93 (4.85)	10.66 (10.99)	34
$[NiL\cdot H_2O]\cdot 3H_2O$	$C_{16}H_{17}N_2O_{13}S_2NaNi$	591.1	408	69	2.58	32.74 (32.51)	3.15 (2.90)	4.98 (4.74)	10.49 (10.85)	31
$[CoL\cdot H_2O]\cdot 3H_2O$	$C_{16}H_{17}N_2O_{13}S_2NaCo$	591.4	412	65	2.67	32.66 (32.50)	2.98 (2.90)	4.83 (4.74)	10.52 (10.84)	33
$[ZnL\cdot H_2O]\cdot 4H_2O$	$C_{16}H_{19}N_2O_{14}S_2NaZn$	597.8	401	68	Dia	31.56 (31.20)	3.19 (3.11)	4.69 (4.55)	10.33 (10.62)	36

[a]Dec. point; [b]Per metal ion at room temperature; [c]Ohm^{-1} cm^2 mol^{-1}

TABLE-2
INFRARED, UV-VISIBLE AND MASS SPECTRAL DATA FOR THE AZO LIGAND AND ITS METAL COMPLEXES

Compound	ν(HO)	ν(C-O)	ν(C=O)	ν(-N=N-)	ν(MN)	ν(M-O)	Molecular ion Found (Calcd.)	λ_{max} (nm) (ε_{max}, M^{-1} cm^{-1})
L	3415 br	1205 m	1680 m	1480 s	-	-	462.9 (462.4)	230 (121100), 330 (14500) 532 (41100)
$[CuL\cdot H_2O]\cdot 2H_2O$	3349 br	1172 m	-	1458 s	640 w	572 w	540.4 (541.9)	235 (118000), 340 (17300), 522 (40500), 665 (1062)
$[NiL\cdot H_2O]\cdot 3H_2O$	3350 br	1166 m	-	1455 s	638 w	563 w	536.2 (537.1)	231 (128400), 336 (18900), 526 (40900), 705 (985)
$[CoL\cdot H_2O]\cdot 3H_2O$	3360 br	1169 m	-	1464 s	634 w	564 w	536.5 (537.3)	230 (117600), 332 (16700), 528 (41600), 692 (964)
$[ZnL\cdot H_2O]\cdot 4H_2O$	3375 br	1184 m	-	1460 s	644 w	576 w	543.3 (543.8)	229 (113500), 343 (17900), 518 (40800), 728 (1003)

assigned to the aromatic naphtholic and phenolic structures. The broad and strong band between 520 and 540 nm was assigned to the azo π-π* transition in the azo ligand, most likely involving extended conjugation. The existence of an n-π* transition in the electronic spectra indicates (330 nm) that the free ligand has a planar conformation in solution, with no rotation of the chelate ring about the bonding azo and hydroxyl group[12].

The UV-visible spectra of the metal-complexes provide additional evidence for the transformations that arise from complexation when compared to the unbound azo ligand and clear differences can be observed between the electronic absorption spectra of the azo ligand and its complexes. Bathochromic shifts were observed in all the metal complexes compared to the free ligand. The absorption peak of azo ligand at 532 nm was slightly shifted toward a lower wavelength in the metal complexes of azo ligand. This indicates that the length of π-electron conjugation was changed due to complex formation. The electronic spectra of all the complexes showed two major bands that are more intense than the corresponding unbound ligand in the region between 518 and 528 nm. These bands are assigned to charge transfer (CT) transitions from the metal to the ligand[13]. We therefore assume that the azo ligand coordinate the metal ions through the oxygens and the azo nitrogens. The electronic spectra of the Co(II) complex, exhibits a band at 675 nm assignable to the *d-d* transition, indicating tetrahedral geometry for cobalt complex. Also the magnetic moment of 2.67 BM is a further indication for the distorted tetrahedral geometry. Detailed analyses of the electronic spectra of all the metal complexes displayed bands

between 665 and 728 nm indicating that a distortion of planar structure of the azo ligand due to the complexation.

Magnetic moments: The magnetic moments of the metal chelates were measured by the Gouy method and diamagnetic corrections were made using Pascal's constants[14]. The magnetic moments of the metal complexes are provided in Table-1. According the magnetic moment calculations, Ni(II), Zn(II), Co(II) and Cu(II) have two, zero, three and one unpaired electrons, respectively. Zinc(II) complex is diamagnetic and other complexes are paramagnetic in character. The magnetic moments of the Ni(II) complexes (2.58 B.M.) were in agreement with the reported values for high-spin tetrahedral complexes. The higher μ_{eff} values exhibited by all complexes, further supports spin conditions with ML·H$_2$O system where high spin arrangement in the ground state. The Cu(II) complex has the value of 1.74 BM. Thus, the magnetic moment value supports a distorted tetrahedral geometry around the Cu(II) metal ion in complex. The magnetic moments of all the complexes were in agreement with the reported values for distorted tetrahedral complexes (Table-1). The IR spectra, elemental analyses and TGA indicate the presence of coordinated water molecules in these complexes. Molecular models indicate that there are no severe steric strains in these complexes as a result of the proposed geometries.

IR spectra: FT-IR spectral data of the azo ligand and its metal complexes were given in Table-2. The IR spectra of the azo ligand displayed a shoulder in a broad band of weak intensity around 2990-2735 cm^{-1}. This band was attributed to the O-H stretch, which is known to shift to lower frequencies as a result of OH···N intramolecular hydrogen bonding[15]. Azo

ligand showed a diagnostic peak in the 3470-3415 cm^{-1} range corresponding to the naphtholic OH and crystalline water molecules. This band was smaller and shifted to lower frequencies (30 cm^{-1}) in the metal complexes due to binding by the oxygen to the metal ions.

The strong bands at 1495 cm^{-1} were due to the C=C stretching of the aromatic ring, while the weak bands at 980 cm^{-1} corresponded to CH deformations. The medium bands in the 1480-1455 cm^{-1} range were assigned to the -N=N- group in the azo ligand and its complexes. The IR spectra of the complexes compared with those of the azo ligand indicate that -N=N- band 1480 cm^{-1} is shifted to the lower values for complexes. These shifted IR values indicate that there is a coordination of the one of the diazo nitrogen to the metal ion. The weak band at 1680 cm^{-1} is due to the C=O stretching vibration corresponded to keto-hydrazone tautomerisation. A weak and broad band at 3140 cm^{-1} which can be attributed to the NH of the -HN-N=C moiety of azo ligand due to the keto-hydrazone tautomerisation[16]. It was also noticed in the spectra of the metal complexes that weak H-N, observed in the azo ligand, disappeared and two strong bands assigned as -N=N- and C-O appeared at low frequency 1464-1455 and 1184-1166 cm^{-1}, respectively. These spectra data show that the metal ions coordinated through hydroxyl oxygen and azo group nitrogen atoms.

According to molecular modeling studies, only one of the diazo nitrogen atoms can be involved in complex formation. The IR spectra of all the metal complexes exhibited broad bands in the 3375-3349 cm^{-1} range that are assigned to coordinated and the crystalline water molecules[17]. The metal complexes also displayed absorption peaks of coordinated water at 800-860 cm^{-1}. The IR spectra of the metal complexes, also showed new bands at 644-634 and 576-564 cm^{-1} assigned to M-N and M-O bonds, respectively[18]. Hence, from the IR spectra, EA, magnetic moments, we conclude that azo ligand is mononuclear and tridentate complex.

^{1}H and ^{13}C NMR spectra: The ^{1}H NMR and ^{13}C NMR spectra of the azo ligand were recorded in DMSO-d_6. The ^{1}H NMR spectrum of azo ligand showed multiplets between 6.4 and 8.6 ppm, assigned to the aromatic ring protons. The other peak at 3.4 ppm was assigned to the H$_2$O molecules. The broad singlet signals at 14.3 and 8.9 ppm may be considered as phenylazo ring OH protons. The singlet at 9.6 ppm may be assigned to the OH proton of naphthalene ring. The peak of the *o*-hydroxyl proton of phenylazo ring was shifted downfield (14.3 ppm) as a result of strong hydrogen bonding between the diazo nitrogen and the hydroxyl proton. A new peak in the spectrum of azo ligand was found at the 14.3 ppm, confirming

the suggested presence of the keto-hydrazone tautomer. The hydrazone peak of azo ligand shifted to 14.3 ppm as a result of the strong hydrogen bonding between hydrazone and the keto forms[19]. This result corroborates to the IR spectra.

In the ^{13}C NMR spectrum of azo ligand, signals between 109.6 and 185.1 ppm are due to the aromatic ring carbons. The relatively high upfield shift of the two carbonyl carbons at 179.3 ppm and 185.1 ppm can be attributed to hydrogen bonding between the diazo nitrogen and hydroxyl carbon of the phenyl and naphthalene rings[20].

Metal ion uptake studies: Metal ion uptake data for the azo ligand was shown in Table-3. The azo ligand bear two sulfonyl groups for improving water solubility. The saturation time was obtained by plotting the per cent of metal ion uptake versus contact time, keeping the initial metal ion concentration fixed at 2500 μg per 25 mL. The effect of the metal ion concentration on the uptake behavior of the ligand was studied in the concentration range between 500 and 2500 μg per 25 mL of metal ions. Interestingly, a leveling effect was not observed at higher concentration due to saturation of available coordination sites. In our work, the optimum pH's for the adsorption of the Cu(II), Zn(II), Ni(II) and Co(II) ions were 5.6, 6.5 and 7, respectively and a high concentration of metal ion enhanced the percentage of loading. The rate of Cu(II) and Zn(II) adsorption of azo ligand were higher than that of both Ni(II) and Co(II). However, the metal ion uptake percentage of ligand was very high at pH = 7 and pH = 6.5 (Table-3). This may be due to the chelating nature of the azo ligand. Additionally, the presence of the hydroxyl groups in the azo ligand may be responsible for a higher uptake percentage of metal ions. The synthesized barium salt of azo ligand could possibly be used for the chelation of heavy metal ions for environmental applications.

Mass spectra: EI-MS was used structural analyses for azo ligand and its metal complexes. The mass spectra of the azo ligand (Fig.3.) and its metal complexes were obtained and the molecular ion peaks are reported in Table-2. All values were in agreement with the formulae of the azo ligand and complexes. The mass spectrum of azo ligand presented a peak corresponding to the molecular ion [M]$^{+}$ at m/e 462.9 (33.3 %) and its elemental composition agreed with the proposed formula, $C_{16}H_{11}N_2NaO_9S_2$ (Table-1). We also obtained evidence for this from the existence of the free base, as could be deduced from the free base peaks at m/e 356.7 (55 %) and 352.6 (97.1 %), which correspond to the naphthalene ring. The major fragmentation appeared to arise from the cleavage of the -N=N- bond in the azo moiety. Mass spectral data are consistent with the formulations [CuL·H$_2$O] which give parent ions at *m/z*

TABLE-3
EFFECT OF PH ON THE ADSORPTION BEHAVIOR OF THE AZO LIGAND FOR
Cu(II), Zn(II), Ni(II) AND Co(II) IN BATCH TECHNIQUE

Metal ion	Metal ion uptake (%) at different pH[a]						
	3.5	4.0	5.0	5.6	6.5	7.0	8.1
Cu(II)	14.2	17.5	36.8	57.9	71.2	68.0	24.3
Ni(II)	13.3	16.9	24.3	28.1	65.3	63.7	22.5
Co(II)	12.8	15.5	22.6	26.3	63.5	63.0	21.4
Zn(II)	15.1	20.6	29.3	32.5	67.4	67.1	23.7

[a]Metal ion concentration, 2500 mg per 25 mL; azo ligand quantity, ligand size, 100 mesh; Temperature 25 °C; contact time, 6 h

TABLE-4
THERMAL DECOMPOSITION OF THE METAL COMPLEXES

Complexes	Dehydration stage					Decomposition stage		
	Temp. range (°C)	Total water % mass loss Found (Calcd.)	Temp. range (°C)	Total water % mass loss Found (Calcd.)[a]	No. of H$_2$O (mol)	Temp. range (°C)	% Mass loss Found (Calcd.)	Final product
[CuL·H$_2$O]·2H$_2$O	75-105	6.3 (6.2)	118-165	9.6 (9.3)	3	410-455	86.6 (86.2)	CuO
[NiL·H$_2$O]·3H$_2$O	70-100	9.3 (9.1)	115-170	12.5 (12.2)	4	405-450	87.7 (87.4)	NiO
[CoL·H$_2$O]·3H$_2$O	75-110	9.4 (9.1)	115-175	12.1 (11.8)	4	390-450	59.5 (59.3)	Co$_3$O$_4$
[ZnL·H$_2$O]·4H$_2$O	70-100	11.9 (11.7)	120-160	14.9 (14.6)	5	395-440	86.7 (86.8)	ZnO

[a]Calc. For the loss of coordinated water molecules

540.4 (calculated value 541.9). The ions in the mass spectra of the Cu complexes, determined in the higher mass number region, are accompanied by [CuL]$^+$ fragments. The mass spectrum of the Cu complex of azo ligand shows a mass fragment corresponding to [C$_{16}$H$_{13}$CuN$_2$NaO$_{10}$S$_2$]$^+$, m/z 522.4 (7.5 %), which loses two water molecule to give fragment [C$_{30}$H$_{10}$Cu$_2$N$_4$Na$_6$O$_{22}$S$_6$]$^+$, m/z 156.1 (9.1 %), followed by a [C$_{10}$H$_4$O$_2$]$^+$ molecule and finally the fragment due to CuO$^+$. The latter is present at m/z 80.1 (16.3 %). In the low mass number region, intense peaks are attributed to the released naphthol ring and its daughter fragments, following well-known pathways. All of the other metal complexes showed similar cleavages.
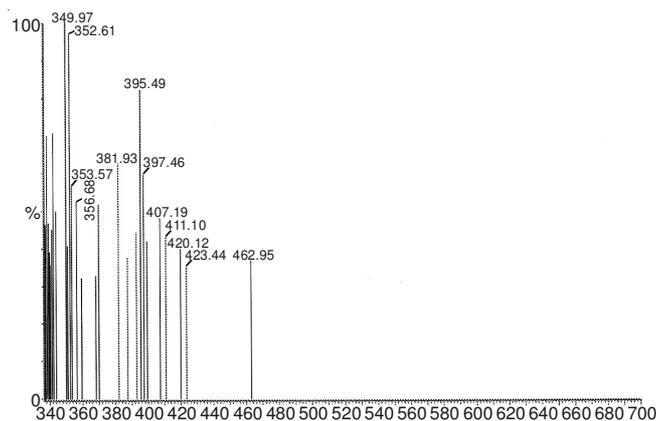

Fig. 3. Mass spectra of the azo ligand

Thermal studies: Thermal behavior of the metal complexes was studied by using thermogravimetric techniques in the 60-900 °C temperature range in nitrogen atmosphere. The data are listed in Table-4. The data indicate that the decomposition of the complexes proceeds in two steps. The complexes lose water molecules between 70 and 170 °C and form metal oxides above 455 °C for the Cu(II), Zn(II), Ni(II) and Co(II) complexes. The coordinated water molecules are eliminated at higher temperatures than the water molecules of hydration. All metal complexes lost hydration water molecules between 70 and 110 °C and then the coordinated water molecule was lost between 115 and 170 °C[21]. The weight losses correspond to loss of one coordinated water molecule in each complex.

The final residues in Ni(II), Zn(II), Cu(II) and Co(II) metal complexes are NiO, ZnO, CuO and Co$_3$O$_4$, respectively. The thermal stabilities of metal complexes are higher than the corresponding azo ligand and the results corroborate some of the assumptions made on the basis of IR spectra and elemental

analyses (vide supra). These metal complexes are probably uses optical data storage due to the high thermal stability.

Conclusion

Analytical data and other studies suggest that the complexes are of the general formula [ML·H$_2$O] where M is Cu(II), Zn(II), Ni(II), or Co(II). Magnetic moment studies showed that all of the complexes possess a distorted tetrahedral geometry. According to the UV-visible analysis, magnetic moment data and IR data, the azo ligand coordinates the metal ion through the phenylazo ring oxygen, the naphthalene ring oxygen and the diazo nitrogen (Fig. 2). All the synthesized compounds possess dye character because of molar extinction coefficients (e) exceeds 40000 m^{-1} cm^{-1}. The synthesized (and precipitated) barium salt of azo ligand could be conveniently used for heavy metal chelation especially at pH = 6.5 and pH = 7. Since the thermal stability of the synthesized metal complexes is higher than 390 °C, these compounds might also find use as optical data storage materials.

REFERENCES

1. F. Huang, Y. Wu, D. Gu and F. Gan, *Dyes Pigments*, **66**, 77 (2005).
2. N. Kabay, E. Erdem, E.Y. Kilincarslan and E.Y. Sari, *Transition Met. Chem.*, **32**, 1068 (2007).
3. G.A. Ibañez and G.M. Escandar, *Polyhedron*, **17**, 4433 (1998).
4. H. Zollinger, Colour Chemistry, Wiley-VCH: Weinheim, edn 3, p. 544 (2003).
5. G.G. Mohamed and M.A.M. Gad-Elkareem, *Spectrochim. Acta A*, **68**, 1382 (2007).
6. J.Y. Park, Y. Hirata and K. Hamada, *Dyes Pigments*, **95**, 502 (2012).
7. R.N. Sah and P.H. Brown, *Microchem. J.*, **56**, 285 (1997).
8. S. Motomizu, M. Oshima and Z. Jun, *Analyst*, **115**, 389 (1990).
9. H. Zollinger, Diazo Chemistry I, Wiley-VCH: Weinheim, p. 306 (1994).
10. M. Tuncel and S. Serin, *Transition Met. Chem.*, **31**, 805 (2006).
11. C.J. Tredwell and C.M. Keary, *Chem. Phys.*, **43**, 307 (1979).
12. N.M. Rageh, A. Mawgoud and H.M. Mostafa, *Chem. Papers*, **53**, 107 (1998).
13. A. Gruger, A. Novak, A. Regis and Ph. Colomban, *J. Mol. Struct.*, **328**, 153 (1994).
14. P.W. Selwood, Magnetochemistry, Interscience Publishers, New York, p. 78 (1956).
15. H. Lampert, W. Mikenda and A. Karpfen, *J. Phys. Chem.*, **100**, 7418 (1996).
16. M. Tuncel and S. Serin, *Synth. React. Inorg. Met. Org. Nano-Met. Chem.*, **35**, 203 (2005).
17. C. Anitha, C.D. Sheela, P. Tharmaraj and S. Johnson Raja, *Spectrochim. Acta A*, **98**, 35 (2012).
18. S. Pinchas, B.L. Silver and I. Laulicht, *J. Chem. Phys.*, **46**, 1506 (1967).
19. A. Lycka and J. Jirman, *Dyes Pigments*, **8**, 315 (1987).
20. M. Ilczyszyn, Z. Latajka and H. Ratajczak, *Magn. Reson. Chem.*, **13**, 132 (1980).
21. S. Alghool, H.F. Abd El-Halim and A. Dahshan, *J. Mol. Struct.*, **983**, 32 (2010).