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The synthesis, characterization, thermal and optical properties of copper, nickel, and vanadyl complexes derived from azo dyes

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Two, novel, tetradentate Schiff-base ligands, namely bis-5-phenylazosalicylaldehyde diethylenetriimine and bis-5-[(4-methoxyphenyl)azo]salicylaldehyde diethylenetriimine, as well as their Cu^{2+}, Ni^{2+}, and VO^{2+} complexes, were synthesized and characterized using elemental analysis, infrared and also UV–Visible spectroscopy, ^{1}HNMR and mass spectra. The thermal stability of the free ligands and the related metal complexes, as determined using differential scanning calorimetry and thermal gravimetric analysis, were found to be thermally stable upto 240–275 °C depending on the type of ligand and the central metal atom. The λ_{max} of the ligands and their transition metal complexes in the region 300–800 nm are discussed. The novel metal complexes offer potential for application as recording media owing to both their absorption spectra in the blue-violet light region and high thermal stability.

1. Introduction

Azo compounds are very important molecules and have attracted much attention in both academic and applied research [1–3]. For example, azo derivatives and their metal complexes are very important pigments for synthetic leather and vinyl polymers. On the other hand, azo compounds are known to be involved in a number of biological reactions, such as inhibition of DNA, RNA, and protein synthesis, nitrogen fixation, and carcinogenesis [4]. Furthermore, high-density optical data storage has been a subject of extensive research in the past decade. In general, cyanine dyes, phthalocyanine dyes, and metal–azo complex dyes are used in the recording layer of DVD-R (Digital Versatile Disc-Recordable) discs. It has been reported that the new technology, which employs 405 nm blue-violet diode lasers, requires a new optical recording medium matching the 405 nm wavelength laser. In comparison with the dyes themselves, metal-azo dyes are more light stable, allow for easier control of the wavelength by selection of the appropriate substituent groups, and have good thermal stability [5–9]. Because of the good thermal stability of azo compounds and the ease with which the absorption band may be tuned by varying the substituents, one of the many applications of azo compounds is in optical data storage.

In other words, the thermal properties and suitable absorption band of azo compounds are essential features in relation to their application as high-density optical recording materials. In a continuation of our interest in the synthesis of azo-based compounds [10–14], we report herein the syntheses and study of the thermal and optical properties of new Schiff-base azo compounds and their copper, nickel, and vanadyl complexes (see Scheme 1).

2. Experimental

2.1. Reagents

All reagents and solvents used were supplied by Merck chemical company and were used without further purification. 5-Phenylazosalicylaldehyde and 5-(4-methoxyphenylazo)salicylaldehyde were obtained as described elsewhere [15].

3. Physical measurements

Elemental (C, H, N) analyses were carried out on a Perkin–Elmer model 240B automated analyzer. Electron impact (70 eV) mass spectra were recorded on a Finnegan-MAT model 8430 GC MS-DS spectrometer. Infrared spectra were recorded in the range 400–4000 cm^{-1} with a Bruker vector 22 FT-IR spectrometer from samples in KBr pellets. Absorption spectra were recorded in the range 300–800 nm

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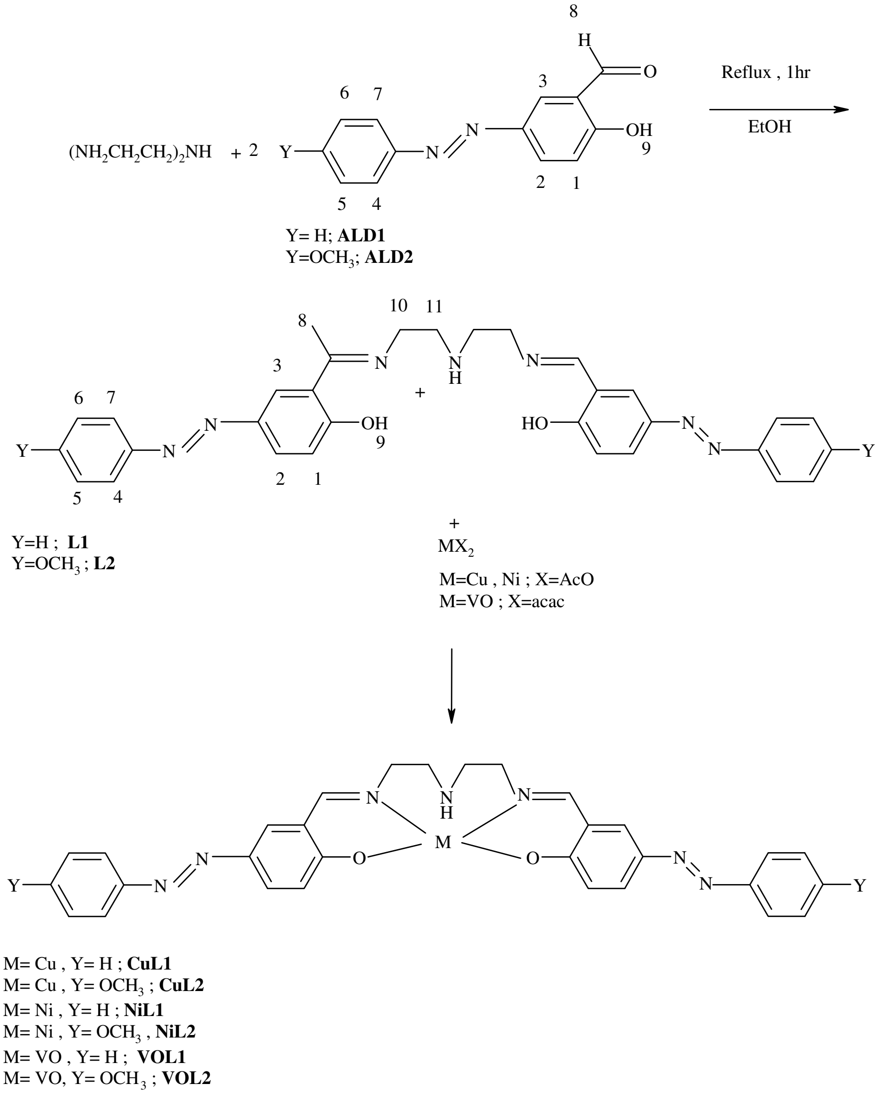

Scheme 1.

on a Shimadzu model 1601 PC UV–Visible spectrophotometer. DSC thermograms of the compounds were obtained on a Mettler-Toledo DSC 822e module, which was calibrated with indium metal ($T = 156.6 \pm 0.3$, $\Delta H = 28.45 \pm 0.6\ \mathrm{J\ g^{-1}}$). Samples of 2–5 mg in solid form were placed in aluminum pans (40 μL) with a pierced lid, and heated or cooled at a scan rate of 10 °C $\mathrm{min^{-1}}$ under a nitrogen flow. TGA was carried out on a Mettler-Toledo TGA 851e apparatus at a heating rate of 10 °C $\mathrm{min^{-1}}$ under a nitrogen atmosphere. ^{1}HNMR spectra were obtained from samples in deuterated chloroform as solvent on a Bruker AC-400 (400 MHz) FT-NMR instrument. All chemical shifts are reported in δ (ppm) relative to tetramethylsilane as an internal standard. Magnetic Susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature using $Hg[Co(SCN)_4]$ as a calibrant.

4. Materials

4.1. 5-Phenylazosalicylaldehyde (ALD1)

This compound was prepared as described in the literature [15]. Yield 65%, mp. 128 °C; yellow powder. ^{1}HNMR (400 MHz, $CDCl_3$): $\delta = 11.25$ (s, H-9), 10.01 (s, H-8), 8.18 (d, $J = 3.2$ Hz, H-3), 8.15 (dd, $J = 3.1, 8.4$ Hz, H-2), 7.87 (dd, $J = 3.1$ Hz, H-4, H-7), 7.11 (d, $J = 8.7$ Hz, H-1), 7.01 (3H, H-5, H-6, H-Y). IR (KBr): $\nu = 3250$ (O–H), 3050 (C–H, aromatic), 1666 (C=O), 1600 (C=C, aromatic), 1481 (N=N), 1105 $\mathrm{cm^{-1}}$ (C–O, phenolic). MS: m/z (relative intensity): 227 (M+1, 12), 226 (M, 25), 121(M-$C_6H_4N_2$, 100). Elemental analysis calcd. (%) for $C_{13}H_{10}N_2O_3$: C 68.97, H 4.42, N 12.39; found: C 68.6, H 4.0, N 11.9.

4.2. 5-(4-Methoxyphenylazo)salicylaldehyde (ALD2)

This compound was prepared as described in the literature [15]. Yield 76%, mp. 120 °C; yellow powder. ^{1}HNMR (400 MHz, $CDCl_3$): $\delta = 11.27$ (s, H-9), 10.02 (s, H-8), 8.12–8.15 (H-2, H-3), 7.90 (dd, $J = 3.2$, 7.12 Hz, H-4, H-7), 7.10 (d, $J = 8.5$ Hz, H-1), 7.02 (dd, $J = 3.5$, 8.4 Hz, H-5, H-6), 3.89 (s, OCH_3). IR (KBr): $\nu = 3182$ (O–H), 3069 (C–H, aromatic), 2929 (C–H, aliphatic), 1660 (C=O), 1600 (C=C, aromatic), 1483 (N=N), 1247 (C–O, ether), 1105 $\mathrm{cm^{-1}}$ (C–O, phenolic). MS: m/z (relative intensity): 257.2 (M+1, 16), 256.2 (M, 37), 241.2(M-CH_3, 20), 121(M-$CH_3OC_6H_4N_2$, 100). Elemental analysis calcd. (%) for $C_{14}H_{12}N_2O_3$: C 65.59, H 4.69, N 10.93; found: C 65.1, H 4.2, N 10.4.

5. Syntheses of the ligands

Two ligands (**L1** and **L2**) were prepared in a similar manner. Firstly, diethylenetriamine (1.339 g, 0.013 mol) and **ALD1**(5.876 g, 0.026 mol) or **ALD2** (6.661 g, 0.026 mol) were condensed by refluxing in absolute ethanol (100 mL) for 1 h. The solution was then left at room temperature, whereupon the ligands were deposited as yellow microcrystals. The microcrystals were collected by filtration, washed with cold absolute ethanol (15 mL), and then recrystallized several times from ethanol/chloroform (1:3, v/v).

5.1. L1

Yield 80%, m.p. 126 °C; yellow powder. ^{1}HNMR (400 MHz, $CDCl_3$): $\delta = 14.01$ (br s, H-9), 8.43 (s, H-8), 7.94 (dd, $J = 2.9$, 8.2 Hz, H-2), 7.83–7.86 (H-3, H-4, H-7), 7.42–7.50 (H-5, H-6, H-Y), 7.00 (d, $J = 8.9$ Hz, H-1), 3.74 (br s, H-10), 3.03 (br s, H-11), 1.25 (br s, NH). IR (KBr): $\nu = 3450$ (O–H), 3248 (N–H), 3050 (C–H, aromatic), 2900–2950 (C–H, aliphatic), 1637 (C=N), 1605 (C=C, aromatic), 1501 (N=N), 1102 cm^{-1} (C–O, phenolic). MS: *m*/*z* (relative intensity): 520.2 (M+1, 15), 519.2 (M, 65), 309 (M–2 × $C_6H_5N_2$, 100). elemental analysis calcd. (%) for $C_{30}H_{29}N_7O_2$: C 69.34, H 5.56, N 18.88; found: C 68.9, H 5.2, N 18.3.

5.2. L2

Yield 87%, mp. 130 °C; yellow powder. ^{1}HNMR (400 MHz, $CDCl_3$): $\delta = 14.04$ (s, H-9), 8.41 (s, H-8), 7.96 (dd, $J = 2.8$, 8.5 Hz, H-2), 7.93–7.83 (H-3, H-4, H-7), 7.13 (d, $J = 7.9$ Hz, H-1), 6.98 (d, $J = 8.1$ Hz, H-5, H-6), 3.92 (s, OCH_3), 3.74 (br s, H-10), 3.03 (br s, H-11), 1.25 (br s, NH). IR (KBr): $\nu = 3423$ (O–H), 3250 (N–H), 3045 (C–H, aromatic), 2835–2907 (C–H, aliphatic), 1637 (C=N), 1601 (C=C, aromatic), 1501 (N=N), 1243 (C–O, ether) 1102 cm^{-1} (C–O, phenolic). MS: *m*/*z* (relative intensity): 580.2 (M+1, 13), 579.2 (*M*, 60), 309(M-2 × $CH_3OC_6H_5N_2$, 100). elemental analysis calcd. (%) for $C_{32}H_{33}N_7O_4$: C 66.30, H 5.70, N 16.92; found: C 65.9, H 5.4, N 16.6.

6. Syntheses of the copper and nickel complexes

Copper and nickel complexes were prepared in a similar manner as previously described by Nejati et al. [10]. Thus, a solution of $Ni(OAc)_2 \cdot 4H_2O$ or $Cu(OAc)_2 \cdot H_2O$ (0.004 mol) in ethanol (10 mL) was added to a solution of the ligand (0.004 mol) in ethanol/chloroform (1:1, v/v) and the resulting mixture was refluxed for 2 h. The obtained solution was then left to stand at room temperature. The copper complexes were obtained as brown microcrystals, while the nickel complexes were obtained as green microcrystals. The microcrystals were collected by filtration, washed with absolute ethanol, and then recrystallized from ethanol/chloroform (1:3, v/v).

6.1. CuL1

Yield 80%, decomposed at 240 °C; brown powder. Elemental analysis calcd. (%) for $C_{30}H_{27}N_7O_2Cu$: C 62.01, H 4.65, N 16.88; found: C 61.5, H 4.2, N 16.4. IR (KBr): $\nu = 3248$ (N–H), 3050 (C–H, aromatic), 2900–2950 (C–H, aliphatic), 1625 (C=N), 1590 (C=C, aromatic), 1515 (N=N), 1102 cm^{-1} (C–O, phenolic).

6.2. CuL2

Yield 85%, decomposed at 255 °C; brown powder. elemental analysis calcd. (%) for $C_{32}H_{31}N_7O_4Cu$: C 59.95, H 4.84, N 15.30; found: C 59.5, H 4.5, N 14.9. IR (KBr): $\nu = 3250$ (N–H), 3050 (C–H, aromatic), 2900–2950 (C–H, aliphatic), 1625 (C=N), 1590 (C=C, aromatic), 1515 (N=N), 1245 (C–O, ether), 1102 cm^{-1} (C–O, phenolic).

6.3. NiL1

Yield 80%, decomposed at 245 °C; green powder. elemental analysis calcd. (%) for $C_{30}H_{27}N_7O_2Ni$: C 62.53, H 4.69, N 17.02; found: C 62.1, H 4.2, N 16.6. IR (KBr): $\nu = 3250$ (N–H), 3050 (C–H, aromatic), 2848 (C–H, aliphatic), 1620 (C=N), 1590 (C=C, aromatic), 1520 (N=N), 1245 (C–O, ether), 1102 cm^{-1} (C–O, phenolic).

6.4. NiL2

Yield 80%, decomposed at 265 °C; green powder. elemental analysis calcd. (%) for $C_{32}H_{31}N_7O_4Ni$: C 60.41, H 4.88, N 15.42; found: C 60.0, H 4.5, N 15.1. IR (KBr): $\nu = 3250$ (N–H), 3050 (C–H, aromatic), 2926 (C–H, aliphatic), 1620 (C=N), 1598 (C=C, aromatic), 1500 (N=N), 1245 (C–O, ether), 1102 cm^{-1} (C–O, phenolic).

7. Syntheses of the vanadyl complexes

Vanadyl complexes were prepared in a similar manner as previously described by Nejati et al. [10]. Thus, $VO(acac)_2$ (0.004 mol) was added to a hot solution of the ligand (0.004 mol) in dichloromethane (70 mL) containing a few drops of triethylamine and the resulting mixture was refluxed for 1 h. A yellow precipitate separated, which was collected by filtration, washed with dichloromethane and diethyl ether, and recrystallized from ethanol/chloroform (1:3, v/v).

7.1. VOL1

Yield 80%, decomposed at 260 °C; yellow powder. elemental analysis calcd. (%) for $C_{30}H_{27}N_7O_3V$: C 61.65, H 4.62, N 16.78; found: C 61.2, H 4.3, N 16.4. IR (KBr): $\nu = 3250$ (N–H), 3050 (C–H, aromatic), 2926 (C–H, aliphatic), 1620 (C=N), 1598 (C=C, aromatic), 1500 (N=N), 1102 (C–O, phenolic), 843 cm^{-1} (V=O).

7.2. VOL2

Yield 85%, decomposed at 275 °C; yellow powder. elemental analysis calcd. (%) for $C_{32}H_{31}N_7O_5V$: C 59.63, H 4.81, N 15.22; found: C 59.2, H 4.4, N 14.9. IR (KBr): $\nu = 3250$ (N–H), 3050 (C–H, aromatic), 2926 (C–H, aliphatic), 1620 (C=N), 1598 (C=C, aromatic), 1500 (N=N), 1245 (C–O, ether), 1102 (C–O, phenolic), 845 cm^{-1} (V=O).

8. Results and discussion

8.1. Synthesis

The Schiff-base ligands, **L1 and L2**, were synthesized in a two-step process. In the first step, salicylaldehyde was coupled with the

Table 1
Melting points, enthalpy changes, decomposition temperatures, magnetic moments (μ_{eff}) and absorption spectral data of Schiff-base ligands and related metal complexes.

Compound	mp.[a]/°C	ΔH[b]/kJ mol^{-1}	T_d/°C[c]	λ_{max}[d]/nm	μ_{eff}(B.M.)
L1	126	41.3	230	350	
L2	130	39.6	245	362	
CuL1			240	355	1.73
NiL1			245	375	
VOL1			260	382	1.69
CuL2			255	370	1.72
NiL2			265	390	
VOL2			275	397	1.70

[a] Data obtained from first DSC cycle. 10 °C/min under N_2 gas.
[b] Data obtained from first DSC cycle. 10 °C/min under N_2 gas.
[c] Decomposition temperatures, data obtained from TGA. 10 °C/min under N_2 gas.
[d] In chloroform.

diazonium chloride obtained from 4-methoxyaniline or aniline. Subsequent reaction of the thus formed 5-(4-methoxy-phenylazo)salicylaldehyde or 5-phenylazosalicylaldehyde with diethylenetriamine (Scheme 1) by refluxing in absolute ethanol using a few drops of acetic acid as catalyst afforded the Schiff-base ligands, which were purified by repeated crystallization from an ethanol/chloroform mixture.

It is well known that salicylidene imines (ortho-hydroxy Schiff bases) are able to form intramolecular hydrogen bonds (OH….N=CH) with the possibility of ground- and excited-state proton transfer. This process is the basis of the photo- and thermo-chromic properties of these compounds [16–18].

5-(4-Methoxyphenylazo)salicylaldehyde (**ALD2**), 5-phenylazosalicylaldehyde (**ALD1**), and the Schiff-base ligands (**L1** and **L2**) were characterized by IR and ^{1}HNMR spectroscopy, mass spectrometry, and elemental analyses. The copper, nickel, and vanadyl complexes were characterized by C, H, N elemental analysis, magnetic measurements, IR spectroscopy and UV analyses. Some physical and characterization data for the ligands and complexes are given in the Experimental Section. The elemental analyses, spectroscopic data and magnetic measurements for the new compounds are in good agreement with the proposed formula.

The mass spectrum of **ALD1** showed a molecular ion peak at *m*/*z* 226 which is equivalent to its molecular weight. In addition, the fragment peaks at *m*/*z* 121(parent peak) is due to the cleavage of $C_6H_5N_2$. In case of **ALD2** the molecular ion peak at *m*/*z* 256.2 is attributed to $C_{14}H_{12}N_2O_3$. The peaks at 241.2 and 121(parent peak) are assigned to the cleavage of CH_3 and $CH_3OC_6H_5N_2$ respectively. The mass spectrum of **L1** showed a molecular ion peak at *m*/*z* 519.2 which is equivalent to its molecular weight. In case of **L2** the molecular ion peak at *m*/*z* 579.2 is attributed to $C_{32}H_{33}N_7O_4$. In addition, the fragment peak at *m*/*z* 309(parent peak) for **L1** and **L2**

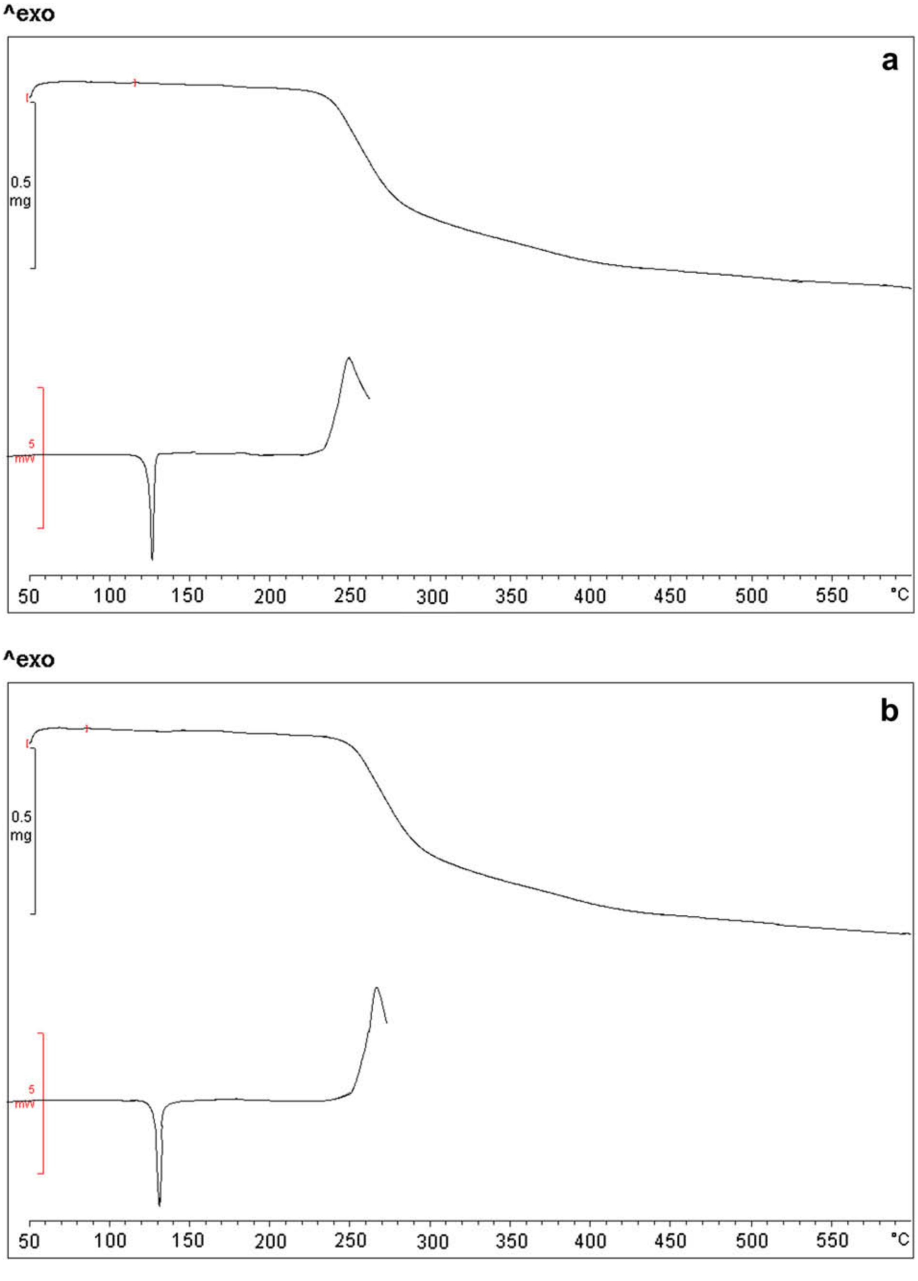

Fig. 1. TGA (above) and DSC (below) curves of the ligands: a) **L1** and b) **L2**.

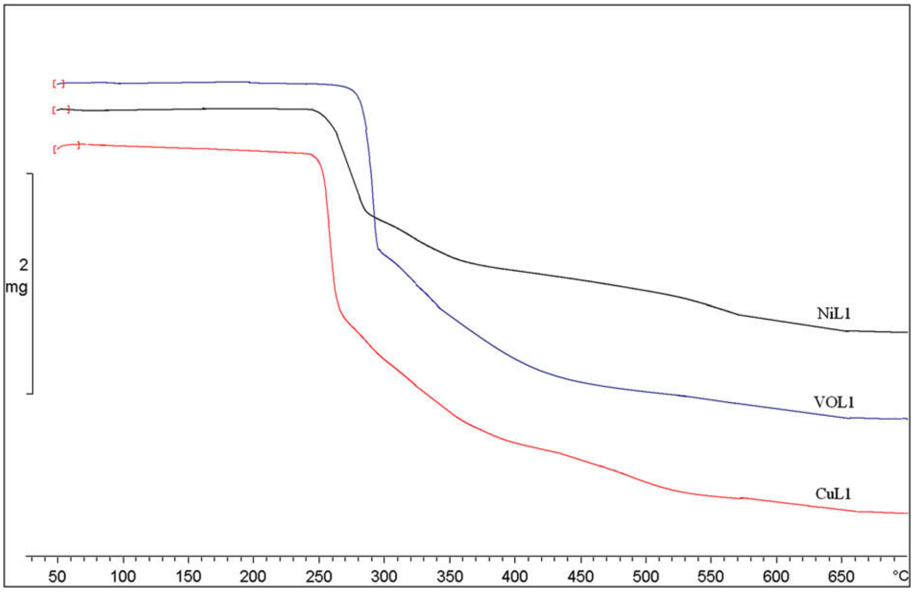

Fig. 2. TGA thermograms of the **CuL1**, **NiL1**, and **VOL1** complexes.

is due to the cleavage of two $C_6H_5N_2$ and two $CH_3OC_6H_5N_2$ moieties respectively.

The signal at 11.25 and 11.27 ppm in the ^{1}HNMR spectra of azo-linked salicylaldehyde precursors (**ALD1** and **ALD2**) is assigned to the OH protons. The CHO protons of **ALD1** and **ALD2** display a signal at 10.01 and 10.02 ppm. In addition to this the multiple signals around 7.01–8.18 ppm are due to aromatic protons. In case of **ALD2**, an additional signal at 3.89 ppm is attributed to OCH_3. The broad signal at 14.01 and 14.04 ppm in the ^{1}HNMR spectra of **L1** and **L2** is assigned to the OH protons. The CH = N protons of **L1** and **L2** exhibit a singlet resonance at 8.43 and 8.41 ppm respectively. Besides, signals for the = NCH_2 and CH_2NH protons of the Schiff-base ligands display a broad singlet at 3.74 and 3.03 ppm respectively. The presence of broad singlet instead of triplet signals in these protons is due to the quadrupolar broadening caused by the spin quantum number of nitrogen atom. Finally, The NH proton of the Schiff-base ligands shows a broad singlet at 1.25 ppm. The ^{1}HNMR proton numbering scheme of **ALD1**, **ALD2**, **L1** and **L2** are represented in Scheme 1. A strong band is observed in the IR spectra of **ALD1** and **ALD2** in the region 1660–1666 cm^{-1} which can be assigned to the ν(C=O) group. The total absence of ν(C=O) absorption in the IR spectra of L1 and L2 together with the presence of new ν(C=N) absorption at 1637 cm^{-1} clearly indicated that a new Schiff-base ligand had formed in each case. Comparison of the IR spectra of the metal complexes with those of the free ligands shows that the stretching frequency of the C=N bond is shifted to lower wavenumbers (15–17 cm^{-1}) after coordination. This shift is due to reduction of the double-bond character of the C=N bond as a result of coordination of the nitrogen to the metal center, and is in agreement with the results obtained for other similar complexes described previously [10,19,20]. On the other hand, the absence of the OH band of the free ligands in the spectra of the metal

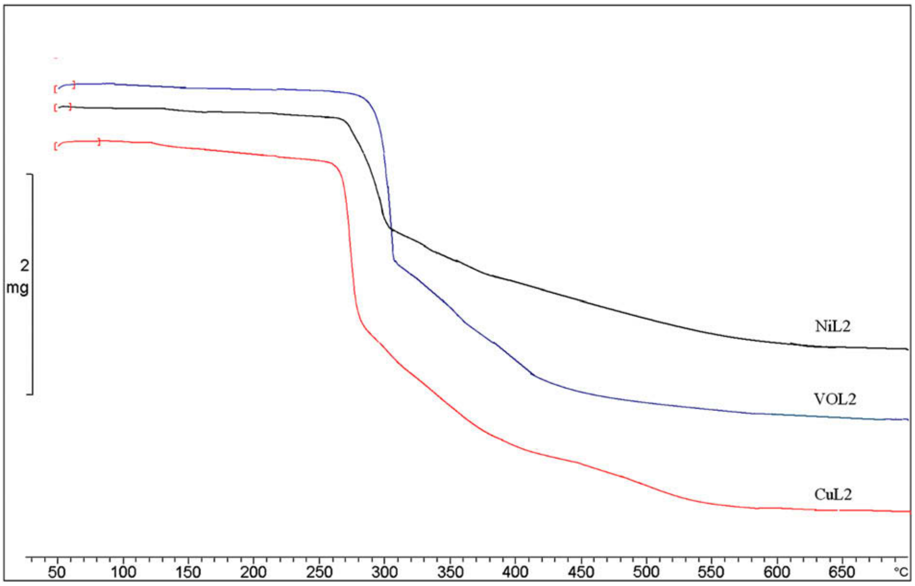

Fig. 3. TGA thermograms of the **CuL2**, **NiL2**, and **VOL2** complexes.

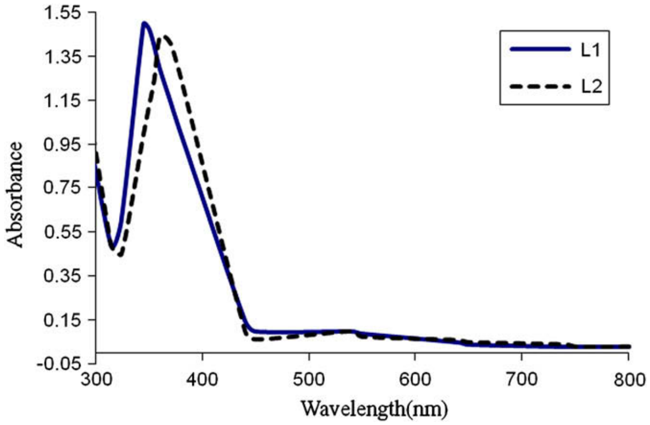

Fig. 4. Absorption spectra of **L1** and **L2** in $CHCl_3$.

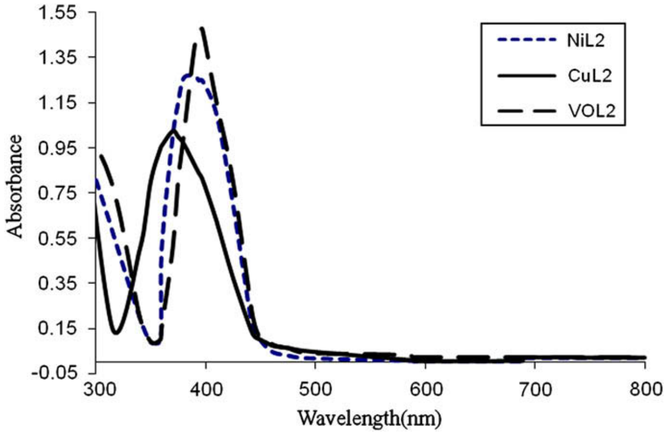

Fig. 6. Absorption spectra of **CuL2**, **NiL2**, and **VOL2** in chloroform.

complexes indicates deprotonation of the OH group and coordination to the metal ion as –O–. The IR spectra of metal complexes show no shift in the position of the N–H band in comparison to the IR spectra of the free ligands. Based on these observations and the elemental analyses, we conclude that the metal complexes are four-coordinate via ONNO of the ligand and have a 1:1 metal-to-ligand stoichiometry.

It is well known that the Ni(II) coordination geometry in salen-type ligands is usually square planar [21,22]. We recently reported the crystal structure of [bis(5-phenylazo-salicylaldehyde)trimethylenediiminato]copper(II), which has a similar ONNO coordination environment to that of the title complexes of this work. It is suggested that the Cu(II) coordination is square planar or nearly square planar on the basis of the similarity of its coordination environment to that of a recently reported copper(II) complex [21]. VO complexes with salen-type ligands can give rise either to a monomeric structure [22–24] with square-pyramidal coordination geometry or to polymeric structures [25–27] with [V=O···V=O] interactions, which afford a distorted octahedral geometry. Based on our knowledge, the V=O stretching frequency of the polymeric structure shows a band in the 840–890 cm^{-1} range but the monomeric structures have an absorption at 950–990 cm^{-1}. However, on the basis of the position of the V=O band in the IR spectra [24–27], we can distinguish between complexes that are monomeric or polymeric in nature. In this work, the VO complexes showed ν(V=O) at 845 cm^{-1}, which indicated a polymeric structure with octahedral coordination of the vanadyl complex. These results are similar to those obtained for the bis(alkylphenylazo)-*N*,*N*-salicylidenediiminato VO(IV) complexes reported by Aiello and co-workers [28]. Based On literature data, coordination of oxo-oxygen atom to an adjacent vanadium atom weakens the V=O bond and lowering the V=O stretching frequency in the polymeric tetradentate Schiff-base–oxovanadium(IV) complexes [29,30].

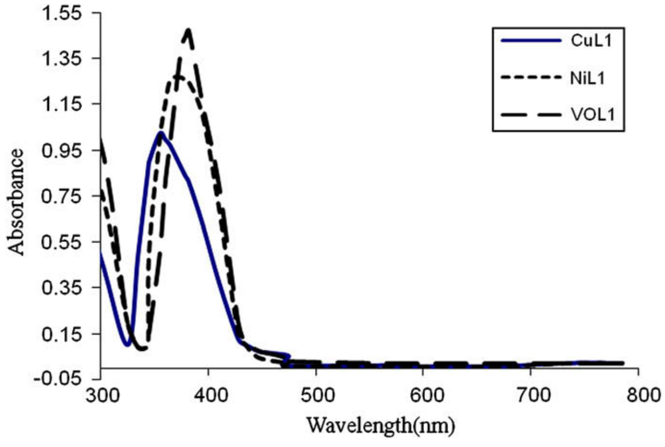

Fig. 5. Absorption spectra of **CuL1**, **NiL1**, and **VOL1** in chloroform.

The magnetic moments of complexes (as B.M.) were measured at room temperature and diamagnetic corrections were calculated from Pascal's constants [31]. Nickel(II) complexes have diamagnetic character, and confirm that the complexes have a square-planar geometry. The magnetic moment values of the Cu^{2+} and VO^{2+} complexes (see Table 1) lie in the range observed for complexes with one unpaired spin (1.69–1.73 Bohr magneton).

8.2. Thermal properties and electronic spectra

Thermogravimetric (TGA) and differential scanning calorimetric (DSC) curves for the ligands are presented in Fig. 1a and b. The DSC curves are indicative of melting processes at 126 and 130 °C for **L1** and **L2**, respectively, followed by exothermic decomposition processes.

It can clearly be seen that the TGA curves of the two compounds do not show any mass losses up to 200 °C, which indicates the thermal stability of these ligands and that no water molecules were incorporated in the samples. The TGA curves indicate that the ligands **L1** and **L2** start to decompose at 230 and 245 °C, respectively. Comparison of the T_d (decomposition temperatures) of the ligands shows that **L2** decomposes later than **L1**.

None of the metal complexes showed a melting process and decomposed directly from the solid state, as detected by exothermic peaks in the DSC trace. The TGA thermograms of the metal complexes of **L1** and **L2** are presented in Figs. 2 and 3, respectively. It can clearly be seen that the TGA curves of all of the metal complexes do not display any mass losses up to 200 °C, which again indicates that no water molecules were incorporated in the samples. As the temperature is increased, the TGA curves of **CuL1**, **NiL1**, **VOL1**, **CuL2**, **NiL2**, and **VOL2** exhibit sharp decompositions at about 240, 245, 260, 255, 265, and 275 °C, respectively, which may be due to the loss of the ligands of **L1** and **L2**. These data indicate that all of the synthesized complexes have good thermal stability; they are amenable to the production of a small and sharp recording mark edge in a DVD-R application because of their higher and sharper thermal decomposition threshold [32]. Comparison of the ligands and the metal complexes showed the metal complexes are more thermally stable than the azo dyes, decomposing at temperatures that were 10–30 °C higher. Furthermore, the vanadyl complexes are more thermally stable (10–20 °C) than the nickel and copper complexes. This fact can be related to the polymeric structure of these complexes. In addition, the TGA thermograms show that the methoxy-containing complexes have a higher thermal stability (15–20 °C) than the metal complexes without a methoxy group. Figs. 4–6 depict the absorption spectra of **L1**, **L2**, and their metal complexes, respectively, in chloroform, over the wavelength range 300–800 nm. It can be seen that the main absorption peaks of **L1** and **L2** are at 350 and 362 nm, respectively. These bands appear as absorption maxima with high extinction coefficients and are attributed to $\pi \rightarrow \pi^*$ transitions of the respective compounds [33]. The results indicate that λ_{max} of **L1** in **CuL1**, **NiL1**, and **VOL1** is red-shifted to around 355, 375, and 382 nm, respectively. Similarly, λ_{max} of **L2** in **CuL2**, **NiL2**, and **VOL2** is red-shifted to around 370, 390, and 397 nm, respectively. In view of the strong absorptions of the complexes in the near-ultraviolet region, these features cannot be ascribed to d–d electron transitions of the Cu^{2+}, Ni^{2+}, and VO^{2+} ions, which are generally too weak and may easily be obscured by the strong absorption band of the azo ligand. Therefore, the obvious bathochromic effect seen for the transition metal azo complexes most probably arises from the energy change of the intense $\pi \rightarrow \pi^*$ transition of the conjugated chromophore due to chelation of the transition metal ions by the organic ligands (**L1**, **L2**) [34]. Thermal analyses and absorption spectral data of Schiff-base ligands and related VO^{2+}, Ni^{2+} and Cu^{2+} complexes are tabulated in Table 1.

From Figs. 5 and 6, it can clearly be seen that the ability of the metal ions to induce red shifts decreases in the order $VO^{2+} > Ni^{2+} > Cu^{2+}$. The result can be explained as follows: after coordination of the transition metal ions by the phenolate form of the hydroxyl oxygen and the imine nitrogen atoms of the azo ligands, the azophenolic group causes a change in electron density shift towards the aromatic ring. This increases the dipole moment, which ultimately leads to a bathochromic shift due to the stabilization of the photoexited state more than the ground state [35]. Furthermore, the oxygen atom of phenolate group could more easily donate unbonded electron density to the π-electron system, thereby increasing the effective conjugation and π-delocalization. Consequently, all of the prepared complexes showed a red shift of the absorption peaks of the ligands [36]. The greater ability of VO^{2+} to induce red shifts in comparison to the two other metal ions is due to the presence of the V=O bond, which can produce more effective conjugation and delocalization of the π-electrons and hence decrease the energy of the intense $\pi \rightarrow \pi^*$ transition.

9. Conclusion

In this research work, we have prepared a series of Cu^{2+}, Ni^{2+}, and VO^{2+} complexes (1:1) derived from tetradentate Schiff-base azo-dye ligands, namely bis-5-phenylazo-salicylaldehyde diethylenetriimine (**L1**) and bis-5-[(4-methoxyphenyl)azo] salicylaldehyde diethylenetriimine (**L2**). The thermal stabilities of these compounds were found to decrease in the order: **VOL2** > **NiL2** > **VOL1** > **CuL2** > **NiL1** > **CuL1** > **L2** > **L1**, which may be attributed to the specific chemical structures of the ligands and metal complexes. On the basis of literature data, compounds that are thermally stable up to 250 °C and give rise to an absorption band near 405 nm are suitable for use as recording dyes [30,32]. Thus, on the basis of their high thermal stability, sharp thermal decomposition threshold, and suitable absorption spectra in the blue-violet light region, we conclude that the metal complexes reported here may be potentially useful as high-density optical recording media.

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