Dyes and Pigments 98 (2013) 557-564

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Azo-azomethine dyes with N, O, S donor set of atoms and their Ni(II) complexes: Synthesis, characterization and spectral properties



PIGMENTS

Hamid Khanmohammadi^{a,*}, Khatereh Rezaeian^a, Mostafa M. Amini^b, Seik Weng Ng^c

^a Department of Chemistry, Faculty of Science, Arak University, Arak 38156-8-8349, Iran

^b Department of Chemistry, Shahid Beheshti University, G.C., Tehran 198396311, Iran

^c Department of Chemistry, University of Malaysia, 50603 Kuala Lumpur, Malaysia

ARTICLE INFO

Article history: Received 15 January 2013 Received in revised form 27 March 2013 Accepted 28 March 2013 Available online 12 April 2013

Keywords: Azo-azomethine Azo dye Fluorescence Nickel(II) complexes Thermal properties X-ray structure

1. Introduction

Aromatic azo compounds are key chromophores in the chemical industry as dyes and pigments, food additives, indicators, radical reaction initiators and therapeutic agents [1–4]. They are known to be involved in various fields such as dyeing of textile fibers, coloring of different materials like wood, wool, leather, metal foil and plastic, biological and medical investigations and even the organic synthesis [5,6]. Moreover, azobenzenes can be advanced into materials for nonlinear optics, optical storage media, chemosensors, liquid crystals, photochemical molecular switches, nanotubes and in manufacture of protective eye glasses and filters [7–11].

Recently, considerable effort has been drawn toward azo compounds containing Schiff-base ligands due to their mixed soft-hard donor character (O, N and S donor sites), versatile coordination behavior [12,13], diverse pharmacological properties [14,15] and optical and thermal properties [16–18]. Metal-azo complexes are currently being involved as recording layers in a number of highdensity optical storage systems such as blue-ray discs (BDs) and high density DVDs (HD-DVDs) [19,20]. Aforementioned systems employ blue-laser diodes ($\lambda = 405$ nm) with a shorter wavelength,

ABSTRACT

New azo-azomethine dyes, L^1-L^3 , with N₂S₂O₂ donor set of atoms have been synthesized via condensation reaction of 1,2-bis(2-aminophenylthio)ethane with 5-(4-X-phenyl)-azo-salicylaldehyde (X = Cl, OMe and Me). The new dyes were characterized by IR, UV–Vis, ¹H NMR and fluorescence spectroscopy as well as mass spectrometry and elemental analysis. Mononuclear nickel(II) complexes of the dyes have been also prepared. The crystal structure of [NiL¹]·0.5H₂O was determined by single-crystal X-ray diffraction. The thermal analysis data indicate that all prepared dyes, L^1-L^3 , are thermally stable up to 320 °C. The fluorescence behavior of the prepared complexes have been also investigated and compared to those of L^1-L^3 .

© 2013 Elsevier Ltd. All rights reserved.

which can write smaller bits and thus increase the data storage capacity to 15–100 G bytes, enough to afford compatibility with high-definition television (HDTV) [21,22]. Recently, some new metal-azo complexes, which have absorption bands in the blue-violet light region (350–450 nm) and have good solubility in many solvents, have been proposed for potential applications in high-density recordable optical recording media [23,24]. Furthermore, transition metal complexes of azo-azomethine compounds have been targeted because of their impressive chemical and physical properties. In comparison with free ligands, metalized azo-azomethines are more optically stable, allow for easier control of the absorption wavelength and have good thermal stability [25–27].

In view of the foregoing discussion and the continued interest in coordination chemistry, our present work describes the preparation and properties of three new acyclic azo-azomethine dyes containing $N_2S_2O_2$ donor set of atoms derived from condensation reaction of 1,2-bis (2-aminophenylthio)ethane with 5-(4-substituted-phenyl)-azo-salicyladehyde, Fig. 1, along with their nickel(II) complexes. The prepared compounds have been characterized by spectroscopic methods as well as elemental analysis. The crystal structure of $[NiL^1] \cdot 0.5H_2O$ was determined by single-crystal X-ray diffraction and results showed that the geometry of the coordination sphere of Ni(II) is a slightly distorted octahedral. Thermal properties of the prepared dyes and their complexes were also examined by thermal analysis (TGA-DTA). Furthermore,



^{*} Corresponding author. Tel.: +98 861 2777401; fax: +98 861 4173406. *E-mail address*: h-khanmohammadi@araku.ac.ir (H. Khanmohammadi).

^{0143-7208/\$ –} see front matter \odot 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.dyepig.2013.03.023



 L^1-L^3

Fig. 1. Synthesized azo-azomethine ligands.

fluorescence behavior of azo-azomethine dyes and their Ni(II) complexes has been evaluated. The results indicate that fluorescent emissions of the dves and their complexes are dependent on the substituent groups on the extended conjugated backbone.

2. Experimental

2.1. Materials

All reagents and solvents involved in synthesis were of analytical grade and used as received without further purification. Salicylaldehyde, p-methylaniline, p-chloroaniline, p-anisidine, 2aminothiophenol and 1,2-dibromoethane were obtained from Aldrich and Merck. Azo-coupled salicylaldehyde precursors, 1 and 3, were prepared according to the well-known literature procedure [28].

2.2. Instrumentation

¹H NMR spectra were recorded on a Bruker AV 300 MHz spectrometer. FT IR spectra were recorded as pressed KBr discs, using Unicom Galaxy Series FT IR 5000 spectrophotometer in the region of 400–4000 cm⁻¹. Melting points of all new compounds were determined on Electrothermal 9200 apparatus. Thermal analyses were performed on a DuPont 2000 and a Perkin-Elmer Thermogravimetric Analyzer TGA/DTA 6300 instruments. Elemental analyses were performed on a Vario EL III elemental analyzer. Electronic spectral measurements were carried out using Perkin-Elmer Lambda double beam spectrophotometer in the range 300-900 nm. Fluorescence spectra were recorded using Perkin-Elmer LS50 luminescence spectrophotometer.

2.3. X-ray crystal structure determination

Vapor diffusion of diethyl ether into a solution of $[NiL^1] \cdot 0.5H_2O$ in chloroform/methanol (4:1) afforded brown crystals suitable for study by X-ray crystallography. Crystal data were collected on a Bruker SMART APEX diffractometer at room temperature [29,30] using graphite-monochromated Mo K_a radiation. Cell refinement and data reduction were carried out with the use of the program SAINT [31]. An absorption correction was applied using SADABS [32]. The structure was solved using direct methods with SHELXS-97 [33] and refined by full-matrix procedures using SHELXL-97 [34]. Details of the X-ray experiments and crystal data are summarized in Table 1.

2.4. Synthesis

2.4.1. 1,2-Bis(2-aminophenylthio)ethane

This was prepared by modification of a literature procedure [35]. A mixture of 2-aminothiophenol (12.52 g, 0.10 mol) and sodium hydroxide (4.00 g, 0.10 mol) in deionized water (60 mL) was heated to reflux for 30 min. The mixture was allowed to cool to 60 °C, and 1,2-dibromoethane (9.40 g, 0.05 mol) was added dropwise over a period of 30 min. The mixture was then heated to reflux for 2 h. After cooling to room temperature, the reaction mixture was extracted with chloroform. The organic layer was dried over anhydrous MgSO₄ and then evaporated to dryness. The obtained product was further washed thoroughly with diethyl ether and dried under vacuum at room temperature. Yield: 61%, m. p. 75–77 °C (Lit. 77–78 °C [35]). IR (KBr, cm⁻¹); 3358 and 3387 (NH), 1616 and 1479 (C=C_{arom}).

2.4.2. 1-(3-formyl-4-hydroxyphenylazo)-4-methoxybenzene, 2

Salicylaldehyde (1.22 g, 10 mmol) was dissolved in water (20 mL) containing sodium hydroxide (0.40 g, 10 mmol) and sodium carbonate (4.24 g, 40 mmol) over a period of 30 min at 0 °C. The resulting solution was added slowly to a diazonium solution of panisidine (1.23 g, 10 mmol) in hydrochloric acid/water (9/4, 13 mL) at 0–5 °C. The mixture was stirred for 1 h at 0 °C and then allowed to warm slowly to room temperature. The product was collected by vacuum filtration and washed with NaCl solution (100 mL, 10%). The obtained solid was dried under vacuum at 80 °C overnight. Yield: 95%, m. p. 98–100 °C. ¹H NMR (DMSO-d₆, 300 MHz, ppm): δ 3.80 (s, 3H), 6.27 (d, 1H, J = 9.5 Hz), 7.01 (d, 2H, J = 8.8 Hz), 7.65 (m, 3H), 7.80 (d, 1H, J = 2.8 Hz), 10.06 (s, 1H). IR (KBr, cm⁻¹); 1663 (CHO), 1599 (C=C), 1580 (phenol ring), 1501, 1472 (N=N), 1281 (C-O), 1246,

Table 1	
---------	--

Table 1						
Crystal,	experimental	and	refinement	data	for	I.

Complex	[Ni L¹]·0.5H ₂ O
Empirical formula	C40H29Cl2N6NiO2.5S2
Formula weight	827.42
System, space group	Monoclinic, $P 2_1/c$
a, Å	9.2357 (7)
<i>b</i> , Å	29.106 (3)
<i>c</i> , Å	14.318 (2)
α, Å	90.0
β , deg	101.111 (10)
γ, Å	90.0
<i>V</i> , Å ³	3776.6 (7)
Ζ	4
Color and shape	Brown, prism
Crystal size (mm)	0.30 imes 0.15 imes 0.05
Wavelength, Å	0.71073
ρ_{calcd} , g cm ⁻³	1.455
F(000)	1700
Temperature, K	295 (2)
$\mu ({\rm mm}^{-1})$	0.812
T _{min} , T _{max}	0.7927, 0.9605
$\theta_{\rm max}$, deg	27.50
Index ranges	$-12 \le h \le 12$
	$-37 \leq k \leq 35$
	$-18 \leq l \leq 18$
Reflections collected	8704
refinement ($F^2 > 0$), NV	
$R^{a}_{,a} W R_{2}^{b}_{,b} S$	0.0877, 0.1808, 1.037
Final shift/error _{max}	0.001
Δho max., min. (e Å $^{-3}$)	0.754, -0.558

 $\overset{a}{\overset{}{\to}} R = \sum ||F_0| - |F_c|| / \sum |F_0| \text{ for } F^2 > 2\sigma F^2. \\ \overset{b}{\overset{}{\to}} w R_2 = [[\sum w (F_0{}^2 - F_c{}^2)^2] / \sum w (F_0{}^2)^2]^{1/2}, \ w = [\sigma^2 (F_0{}^2) + (0.05 F_0{}^2)^2]^{-1}.$

1148, 851 and 766. Anal. Calcd. for $C_{14}H_{12}N_2O_3;$ C, 65.62; N, 10.93; H, 4.72. Found: C, 65.53; N, 10.72; H, 4.58%.

2.4.3. General procedure for the synthesis of azo-azomethine dyes, L^1-L^3

A solution of 1,2-bis(2-aminophenylthio)ethane (0.28 g, 1 mmol) in absolute EtOH (10 mL) was added to a stirred solution of azocoupled precursors, **1–3**, (2 mmol) in absolute EtOH (50 mL) during a period of 30 min at 50 °C. The solution was heated in water bath for 4 h at 80 °C with stirring. The mixture was filtered whilst hot and the obtained solid was washed with hot ethanol (three times) and then with diethyl ether. The resulted product was dried in air.

2.4.3.1. 1,2-bis((4-((4-chlorophenyl)diazenyl)-2-((phenylimino) methyl)phenol)thio)ethane, **L**¹. Yield: 77%, m. p. 238–240 °C. ¹H NMR (DMSO-d₆, 300 MHz, ppm): δ 3.24 (s, 4H), 7.13 (d, 2H, *J* = 8.8 Hz), 7.29–7.51 (m, 8H), 7.63 (d, 4H, *J* = 8.3 Hz), 7.85 (d, 4H, *J* = 8.3 Hz), 7.99 (d, 2H, *J* = 8.8 Hz), 8.26 (s, 2H), 9.08 (s, 2H), 13.73 (br, 2H). IR (KBr, cm⁻¹); 1612 (C=N), 1578 (phenol ring), 1470 (N=N), 1350, 1281(C–O), 1082, 837 and 738. *m*/*z* = 43.0, 57.1, 81.0, 109.0, 145, 207.0, 247.0, 301.0, 368.0, 565.0, 617.0. Anal. Calcd. for C₄₀H₃₀Cl₂N₆O₂S₂: C, 63.07; N, 11.03; H, 3.97; S, 8.42. Found: C, 63.21; N, 10.64; H, 4.32; S, 8.65%. λ_{max} (nm) (ϵ (mol⁻¹ dm³ cm⁻¹)): 359 (48881) in DMF.

2.4.3.2. 1,2-bis((4-((4-methoxyphenyl)diazenyl)-2-((phenylimino) methyl)phenol)thio)ethane, **L**². Yield: 72%, m. p. 258–260 °C. ¹H NMR (DMSO-d₆, 300 MHz, ppm): δ 3.24 (s, 4H), 3.86 (s, 6H), 7.12 (m, 6H), 7.34–7.50 (m, 8H), 7.86 (d, 4H, J = 8.7 Hz), 7.95 (d, 2H, J = 7.9 Hz), 8.22 (s, 2H), 9.08 (s, 2H), 13.50 (br, 2H). IR (KBr, cm⁻¹); 1614 (C=N), 1584 (phenol ring), 1468 (N=N), 1358, 1279 (C–O), 1105, 1067 and 835. m/z = 29.0, 43.0, 57.0, 83.0, 111.0, 140.0, 206.9, 250.0, 316.0, 332.0. Anal. Calcd. for C₄₂H₃₆N₆O₄S₂: C, 67.00; N, 11.16; H, 4.82; S, 8.52. Found: C, 67.11; N, 11.43; H, 4.66; S, 8.42%. λ_{max} (nm) (ϵ (mol⁻¹ dm³ cm⁻¹)): 367 (48265) in DMF.

2.4.3.3. 1,2-bis((4-((4-methylphenyl)diazenyl)-2-((phenylimino) methyl)phenol)thio)ethane, L^3 . Yield: 78%, m. p. 220–222 °C. ¹H NMR (DMSO-d₆, 300 MHz, ppm): δ 2.39 (s, 6H), 3.24 (s, 4H), 7.13 (d, 2H, J = 8.8 Hz), 7.32–7.52 (m, 12H), 7.76 (d, 4H, J = 7.8 Hz), 7.98 (d, 2H, J = 8.8 Hz), 8.24 (s, 2H), 9.09 (s, 2H), 13.56 (br, 2H). IR (KBr, cm⁻¹); 1612 (C=N), 1580 (phenol ring), 1470 (N=N), 1350, 1281 (C–O), 1105, 1067 and 824. m/z = 29.0, 57.0, 85.0, 113.0, 141.0, 207.0, 253.0, 309.0, 365.0, 581.0. Anal. Calcd. for C₄₂H₃₆N₆O₂S₂: C, 69.97; N, 11.66; H, 5.03; S, 8.90. Found: C, 69.55; N, 11.23; H, 4.54; S, 9.04%. λ_{max} (nm) (ε (mol⁻¹ dm³ cm⁻¹)): 357 (47345) in DMF.

2.4.4. General procedure for the synthesis of nickel(II) complexes

A solution of Ni(ClO₄)₂·6H₂O (0.37 g, 1 mmol) in absolute ethanol (10 mL) was added to a suspension of L^1-L^3 (1 mmol) in CHCl₃ (50 mL) over a period of 5 min. The reaction mixture was allowed to stirred for 24 h at 45 °C. The obtained solution was left to

stand at room temperature for several days to give solid product. The resultant product was collected by filtration and washed successively with methanol and then dried in air overnight.

2.4.4.1. [*NiL*¹]·0.5H₂O, *I*. Brown crystals, Yield: 73%, m. p. >270 °C. IR (KBr, cm⁻¹); 1606 (C=N), 1574, 1462, 1342 (C-O), 1153, 1142, 835, 748, 582, 547, 497 and 418. Anal. Calcd. for C₄₀H₂₉Cl₂N₆NiO_{2.5}S₂: C, 58.06; N, 10.16; H, 3.53; S, 7.75. Found: C, 57.58; N, 9.93; H, 3.52; S, 7.33%. λ_{max} (nm) (ε (mol⁻¹ dm³ cm⁻¹)): 415 (42883), 430 (43892) in DMF.

2.4.4.2. [*NiL*²(*ClO*₄)]·*CH*₃OH, **II**. Brown powder, Yield: 81%, m. p. >270 °C. ¹H NMR (DMSO-d₆, 300 MHz, ppm): δ 2.78 (s, 2H), 2.91 (s, 2H), 3.76 (s, 3H), 3.83 (s, 3H), 6.53 (m, 1H), 6.74 (m, 1H), 6.93 (s, 3H), 7.10 (m, 7H), 7.28 (d, 1H, *J* = 7.4 Hz), 7.48 (s, 1H), 7.85 (d, 3H, *J* = 7.4 Hz), 8.03 (m, 4H), 8.21 (s, 1H), 9.07 (s, 1H), 10.34 (s, 1H), 11.46 (br, 1H). IR (KBr, cm⁻¹); 1614 and 1599 (C=N), 1579, 1501, 1385, 1356 (C–O), 1151, 1109, 1026, 837, 758, 667, 623, 521, 501, 436 and 415. Anal. Calcd. for C₄₃H₃₉ClN₆NiO₉S₂: C, 54.82; N, 8.92; H, 4.17; S, 6.81. Found: C, 54.67; N, 9.39; H, 4.10; S, 6.98%. λ_{max} (nm) (ε (mol⁻¹ dm³ cm⁻¹)): 393 (46787), 429 (44243) in DMF.

2.4.4.3. [*NiL*³(*ClO*₄)]·*CH*₃OH, **III**. Brown powder, Yield: 83%, m. p. >270 °C. ¹H NMR (DMSO-d₆, 300 MHz, ppm): δ 2.39 (s, 3H), 3.24 (s, 2H), 6.92 (m, 1H), 7.11 (m, 2H), 7.19 (s, 6H), 7.28 (m, 2H), 7.38 (d, 2H, *J* = 7.0 Hz), 7.50 (s, 1H), 7.77 (d, 2H, *J* = 4.6 Hz), 7.97 (s, 4H), 8.16 (s, 1H), 8.25 (s, 1H), 9.10 (s, 1H), 10.36 (s, 1H). IR (KBr, cm⁻¹); 1606 (C=N), 1385, 1356 (C–O), 1292, 1142, 1109, 1016, 831, 760, 667, 623, 551, 503, 470 and 416. Anal. Calcd. for C₄₃H₃₉ClN₆NiO₇S₂: C, 56.75; N, 9.23; H, 4.32; S, 7.05. Found: C, 56.47; N, 9.19; H, 4.26; S, 6.52%. λ_{max} (nm) (ϵ (mol⁻¹ dm³ cm⁻¹)): 403 (40124), 431 (37819) in DMF.

3. Result and discussion

The condensation reaction of 5-(4-X-phenyl)-azo-salicyladehyde (X = Cl, OMe, Me) with 1,2-bis(2-aminophenylthio)ethane in ethanol afforded new azo-azomethines, L^1-L^3 , in good yield. All synthesized compounds, with N, S and O donor set of atoms, are thermally stable solids, intensely colored, soluble in THF, DMF and DMSO. The prepared compounds also exhibited dye character. L^1-L^3 have been used to prepare nickel(II) complexes, I–III. All prepared mononuclear complexes have been characterized by FT IR and UV– Vis spectroscopes and ¹H NMR as far as possible. Also, the crystal structure of I has been determined. Moreover, thermal and spectral properties of L^1-L^3 and their complexes have been reported.

3.1. IR spectra

The position of some of the prominent bands in the IR spectra of L^1-L^3 and their nickel(II) complexes along with their tentative assignments based on extensive data accessible for related compounds [26,36,37] are depicted in Table 2. The total absence of v(C=0) band of azo-coupled salicylaldehyde precursors in the IR

Table 2

Tentative assignments of some selected IR^a frequencies (cm⁻¹) and UV-Vis data of the prepared azo-azomethine ligands and their Ni(II) complexes.

_

^a KBr discs.



Fig. 2. Proposed structure for II and III.

spectra of L^1-L^3 together with the appearance of a new band in the range of 1612–1614 cm⁻¹ clearly indicate that a Schiff-base has formed in each case. On comparing with the literature report [38] the IR spectra of L^1-L^3 exhibit medium bands in the range of 1468–1470 cm⁻¹, corresponds to symmetric N=N stretching mode.

On the other hand, II and III have similar IR spectra but different from that of I. The v(C=N) in the infrared spectrum of I is redshifted by 6 cm^{-1} from that of L^1 . This can be ascribed to the withdrawal of electron density from the nitrogen atom owing to coordination. The v(C-O) (phenolic) in IR spectrum of I appears at 1342 cm⁻¹ and is blue-shifted by 61 cm⁻¹ from that of **L**¹ which is in agreement with the phenolato-O single bonded to Ni(II) ion [39]. The total absence of bands at 1090–1150 cm⁻¹ in the IR spectrum of I implies that the complex has no perchlorate counter ion. The presence of two bands in the infrared spectra of II and III at 1614-1599 and 1612–1606 cm⁻¹, respectively, reveals the presence of two imine bonds. The band at lower frequency, 1599 and 1606 cm^{-1} for **II** and **III**, respectively, owing to the coordination to nickel(II) center and the other band appeared as shoulder close to that of the free ligands [40]. Also, the infrared spectra of II and III show the presence of two phenolic C–O stretching vibrations; one appearing at higher frequency (1356 cm^{-1}) owing to the coordination of one OH group to nickel(II) center and the other appeared at lower frequency close to that of free ligands. Furthermore, in the IR spectra of II and III, the strong vibration band assigned to perchlorate ion is



Fig. 4. Electronic absorption spectra of $L^1 - L^3$ and I - III in DMF.

triple split into three bands, which points the presence of coordinated perchlorate group. In addition, the observed bands at 623 and 667 cm⁻¹ also support the presence of coordinated perchlorate ion [41]. The proposed structures for **II** and **III** are given in Fig. 2 which is also in accordance with data from the ¹H NMR spectra. For all synthesized complexes, the coordination of azomethine nitrogen is also confirmed by the presence of new bands at 436–497 cm⁻¹. Moreover, the Ni–O stretching frequencies for complexes would be at 501–548 cm⁻¹ [22].

3.2. ¹H NMR spectra

The ¹H NMR spectra of $L^{1}-L^{3}$ present the slightly broad signal at 13.50–13.73 ppm, assigned to the OH protons, as was confirmed by deuterium exchange when D₂O was added to DMSO-d₆ solution. The CH=N protons of $L^{1}-L^{3}$ excluded to a singlet at ~9.1 ppm. In addition, the ¹H NMR spectra of $L^{1}-L^{3}$ are dominated by doublets at 7.12–7.63 ppm and at 7.76–7.86 ppm, which belong to the AA'XX' spin system of the *para*-substituted aromatic ring. The doublet pattern of high-field signal is simplified after irradiation of the low-field doublet. The ratio $\Delta\delta/J$ is 8.16, 25.5 and 14.83 for $L^{1}-L^{3}$, respectively.

The ¹H NMR spectrum of **II** reveals the presence of two sets of signals with relative proportions of two sets of azo-coupled units of the ligand (coordinated and uncoordinated). The imine like proton



Fig. 3. The fragments observed in the mass spectra of L¹.



Fig. 5. Molecular structure of I showing displacement ellipsoids at the 50% probability level.

corresponding to the uncoordinated imine group appeared at 9.07 ppm, close to that of L^2 . On the other hand, the coordinated imine hydrogen signal was appeared at 10.34 ppm [42]. Furthermore, the broad signal at 11.46 ppm is attributed to the uncoordinated phenolic OH group. It is interesting to note that a similar pattern of ¹H NMR spectrum was observed for **III**.

3.3. Mass spectra

Mass spectra data of L^1-L^3 were consistent with the molecular ion fragments and support the proposed structures. Some of the fragments observed in the mass spectrum of L^1 are shown in Fig. 3. The peaks observed at m/z = 617, 565 and 301 confirm the formation of the bis-iminated compound. The peaks observed at m/z = 247 in the mass spectra of L^1 can be assigned to the fragment containing chlorine group. The fragmentations observed in the mass spectra of L^2 and L^3 are presented in Section 2 (See Supplementary materials).

3.4. The electronic absorption spectra

The electronic absorption spectra of L^1-L^3 and I-III were recorded in DMF over the 300–900 nm range at room temperature. The results are given in Table 2. The UV–Vis absorption spectra of L^1-L^3 exhibit an absorption maxima at 357–367 nm, Fig. 4, with high extinction coefficients which is attributed to the $\pi \rightarrow \pi^*$ transition involving the π -electrons of the chromophore groups [43]. Also, this band is red shifted after chelation of the free dyes to the Ni(II) ion [19,43]. In addition, the electronic spectra of I-III

Table 3	
Selected bond lengths (Å) and angles (°) for I .	

Bond lengths			
Ni(1) - N(1)	2.045(5)	Ni(1)-O(2)	2.009(4)
Ni(1)-N(4)	2.043(5)	Ni(1)-S(1)	2.424(18)
Ni(1)-O(1)	1.992(4)	Ni(1)-S(2)	2.419(19)
Bond angles			
O(2)-Ni(1)-O(1)	89.81(18)	O(1) - Ni(1) - S(2)	91.67(14)
O(2)-Ni(1)-N(1)	95.02(18)	N(1)-Ni(1)-N(4)	173.57(2)
O(2)-Ni(1)-N(4)	91.21(19)	N(1)-Ni(1)-S(1)	83.79(13)
O(2) - Ni(1) - S(1)	91.64(13)	N(1)-Ni(1)-S(2)	90.44(14)
O(2) - Ni(1) - S(2)	174.28(13)	N(4)-Ni(1)-S(1)	94.43(15)
O(1) - Ni(1) - N(1)	92.36(17)	N(4) - Ni(1) - S(2)	83.30(15)
O(1) - Ni(1) - N(4)	89.27(19)	S(1)-Ni(1)-S(2)	87.25(7)
O(1) - Ni(1) - S(1)	176.00(13)		

depict the very broad band located around 430 nm corresponding to the charge transfer transitions involving the entire molecule, Fig. 4.

3.5. Crystal structure of I

The molecular structure of **I** is shown in Fig. 5 along with the atomic numbering scheme. Selected bond lengths and angles are listed in Table 3. The geometry of the complex is best considered as slightly distorted octahedral. The Ni(II) center is coordinated by the N₂S₂O₂ donor set of atoms where both imine nitrogen atoms are disposed trans to each other (The N(1)–Ni–N(4), S(1)–Ni–S(2) and O(1)–Ni–O(2) angles are 173.57(2), 87.25(7) and 89.81(18)°, respectively). The bond lengths from both coordinated nitrogen atoms to the Ni(II) center are slightly different [Ni–N(1) 2.045(5), Ni–N(4) 2.043(5) Å]. Similar findings were observed for those found from both oxygen and sulfur atoms [Ni–S(1) 2.424(18), Ni–S(2) 2.419(19), Ni–O(1) 1.992(4), Ni–O(2) 2.009(4) Å]. All bond lengths are comparable to corresponding distances reported in literature [44–46].

3.6. Fluorescence properties

The fluorescence emission spectra of L^1-L^3 and I-III were recorded in DMF at room temperature, Fig. 6. As it is shown in Fig. 6, the fluorescence emission of L^1-L^3 appears at *ca*. 520 nm with excitation wavelength 520–530 nm. The fluorescence quantum yields of the dyes were estimated from the following equation [47]:



Fig. 6. Fluorescence emission spectra of the ligands. λ_{ex} (L¹) = 523.5 nm, λ_{ex} (L²) = 530.0 nm, λ_{ex} (L³) = 520.7 nm.

 Table 4

 Thermal analyses data for ligands and their Ni(II) complexes.

Compounds	<i>T</i> _d , °C	Temp. of steps °C	Mass loss % found	Probable % calcd.	Proposed decomposition assignment
L1	336	295-440	52.70	52.94	C ₁₆ H ₁₆ Cl ₂ N ₂ O ₂ S ₂
		440-800	11.71	11.83	C ₆ H ₄ N
L ²	340	270-380	48.18	48.28	$C_{17}H_{19}N_2O_3S_2$
		380-800	15.89	16.09	C ₇ H ₇ NO
L ³	337	295 - 370	46.68	46.11	$C_{16}H_{16}N_2O_2S_2$
		370-800	17.08	16.53	$C_7H_7N_2$
I	344	100 - 270	1.40	1.08	0.5H ₂ O
		270 - 400	28.64	28.73	$C_{14}H_{12}S_2$
		400 - 800	13.75	13.89	C ₇ H ₄ NO
П	249	32-178	3.42	3.40	1CH₃OH
		178 - 420	28.65	28.42	C ₈ H ₈ ClO ₄ S ₂
		420-800	13.04	12.86	C ₇ H ₇ NO
III	295	30-190	3.52	3.52	1CH₃OH
		190-410	29.28	29.42	C ₈ H ₈ ClO ₄ S ₂
		410-800	17.48	17.93	$C_9H_{11}N_2O$

$\Phi_{S} = F_{S}/F_{R} \times A_{R}/A_{S} \times (n_{S}/n_{R})^{2} \times \Phi_{R}$

where Φ_R is the quantum yield of the standard, *A* is the absorbance at the excitation wavelength, *F* is the integrated intensity of the emission spectra, *n* is the refractive index of the solution, index *S* refers to the sample, and *R* denotes the reference. The standard used for measurement of the fluorescence quantum yield was quinine sulfate ($\Phi_R = 0.51$) [47,48]

In the current work, the quantum yields of $L^1 - L^3$ are 0.072, 0.020 and 0.13, respectively which are too low. The azomethine linkage, as well as azo groups, is known to quench the fluorescence of even the most intrinsically fluorescent fluorophores [49,50]. Furthermore, electron-donating and electron-withdrawing groups on the *para*-position of the phenyl ring can drastically alter the electron density and the electron conjugate system of the dyes [50]. This behavior can be interpreted by the presence of fluorescence quenching intra-ligand PET (Photo-induced Electron Transfer) processes, which occur from the conjugated positions of the dyes toward the fluorophores [51]. The electron-donating resonance contribution of the substituent such as a methoxy group may facilitate this process in L^2 to ensure its low fluorescence intensity [52]. Moreover, it is interesting to state that stokes shift values for L^1-L^3 are 161, 153 and 163 nm, respectively, resulting in a negligible overlap between the absorption and emission spectra of the dyes, preventing the re-absorption of the emitted light. These large stokes shifts make unique advantages for detection of emitted light fluorescence in biological applications and are significant for avoiding undesired loses in the optoelectronic devices [49].

In contrast with the fluorescence spectra of L^1-L^3 , fluorescence quenching phenomena are observed in I–III. Quenching of fluorescence of L^1-L^3 after complex formation with transition metal ions can be attributed to the processes such as delocalization of π -



Fig. 7. TGA/DTA curves of (a) L¹ and (b) I.

electrons within system, redox-activity and also electron energy transfer [53].

3.7. Thermal properties

In order to examine the thermal stability of the new compounds, the thermal decomposition studies carried out using thermogravimetry techniques, Table 4. In the present investigation, the heating rates were suitably controlled at 10 °C min⁻¹ under N₂ atmosphere, and the weight loss was measured from 25 °C up to 800 °C.

The TGA/DTA curves of L^1 and I are presented in Fig. 7 (for the other synthesized compounds see Supplementary materials). The TGA curves of L^1-L^3 do not display any mass losses up to 290 °C, which indicate the thermal stability of the ligands and no solvent molecules were incorporated in the samples. Furthermore, for L^1-L^3 the corresponding DTA curves present an endothermic peak without any weight loss exhibiting a physical process which is likely attributed to the melting of prepared compounds. Above 290 °C, the TGA curves show a major loss of weight where the corresponding DTA curve indicates an exothermic peak. The exothermic peak depicts the removal of the ligand framework.

The TGA thermogram of I exhibits a mass loss of 1.40% within the temperature range of 100–270 °C, which corresponds to the loss of water molecule (0.5 mol, calcd. 1.08%). Complexes II and III lose one methanol molecule within the temperature range of 30-190 °C with an estimated mass loss of 3.42% (calcd. 3.40%) and 3.52% (calcd. 3.52%), respectively. It is noteworthy to mention that the thermal decomposition behavior of **I** is quite different from that of **II** and **III**. As the temperature is increased, the TGA curve of **I** exhibits a sudden and sharp decomposition step. This part of the process is accompanied by highly exothermic effect in the DTA curve at 345 °C. However, II and III decompose gradually in the same manner with exothermic effect at 253 and 298 °C, respectively. Above 400 °C, the TGA curves of prepared compounds show a continuous and significant weight loss up to 800 °C. Furthermore, the comparison of decomposition temperature indicates that the I is thermally more stable than the other complexes. This fact can be related to the different structure of I comprised with II and III.

4. Conclusion

In the present work three new bis-iminated azo-azomethine ligands, L^1-L^3 , and their nickel(II) complexes, I–III, have been synthesized and characterized. The prepared ligands have dye-like character since the molar extinction coefficients (ε) were over 30,000 mol⁻¹ dm³ cm⁻¹. The emission spectra revealed that L^1-L^3 are fluorescent in nature, and their fluorescence emission intensity is highly affected by different substitution groups. The order of fluorescence intensity is $L^3 > L^1 > L^2$. Also, further studies exhibited that the complexation to nickel(II) ion quench the fluorescence behavior of $L^1 - L^3$. The prepared dyes are also thermally stable up to 320 °C. In addition, the results indicated that the I is thermally more stable than the other complexes. This fact can be attributed to the specific chemical structure of metal complexes. Suitable electronic absorption spectra of the synthesized complexes were found in blue-violet light absorption at about 350-450 nm. Thus, on the basis of the high thermal stability of the prepared complexes and their suitable absorption spectra in the blue-violet light region, the reported complexes may be potentially good candidates of optical recording media for blue-ray optical information storage.

Acknowledgments

We are grateful to the Arak University for financial support of this work.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.03.023.

References

- Merino E. Synthesis of azobenzenes: the coloured pieces of molecular materials. Chem Soc Rev 2011;40:3835–53.
- [2] Hunger K. Industrial dyes: chemistry, properties, applications. Weinheim: VCH; 2003.
- [3] You W, Zhu H-Y, Huang W, Hu B, Fan Y, You X-Z. The first observation of azohydrazone and cis-trans tautomerisms for disperse yellow dyes and their nickel(II) and copper(II) complexes. Dalton Trans 2010;39:7876–80.
- [4] Sandborn WJ. Rational selection of oral 5-aminosalicylate formulations and prodrugs for the treatment of ulcerative colitis. Am J Gastroenterol 2002;97: 2939–41.
- [5] Koh J, Greaves AJ. Synthesis and application of an alkali-clearable azo disperse dye containing a fluorosulfonyl group and analysis of its alkali-hydrolysis kinetics. Dyes Pigment 2001;50:117–26.
- [6] Bhatti HS, Seshadri S. Synthesis and fastness properties of styryl and azo disperse dyes derived from 6-nitro substituted 3-aryl-2-methyl-4(3H)-quinazolinone. Color Technol 2004;120:151–5.
- [7] Li XY, Wu YQ, Gu DH, Gan FX. Spectral, thermal and optical properties of metal(II)–azo complexes for optical recording media. Dyes Pigment 2010;86: 182–9.
- [8] Li XY, Wu YQ, Gu DH, Gan FX. Optical characterization and blu-ray recording properties of metal(II) azo barbituric acid complex films. Mater Sci Eng B 2009;158:53-7.
- [9] Feringa BL, van Delden RA, Koumura N, Geertsema EM. Chiroptical molecular switches. Chem Rev 2000;100:1789–816.
- [10] Banerjee IA, Yu L, Matsui H. Application of host-guest chemistry in nanotubebased device fabrication: photochemically controlled immobilization of azobenzene nanotubes on patterned α-CD monolayer/Au substrates via molecular recognition. J Am Chem Soc 2003;125:9542–3.
- [11] Crano JC, Guglielmetti RJ. Organic photochromic and thermochromic compounds. New York: Plenum Press; 1999.
- [12] Dinçalp H, Toker F, Durucasu İ, Avcıbaşı N, Icli S. New thiophene-based azo ligands containing azo methine group in the main chain for the determination of copper(II) ions. Dyes Pigment 2007;75:11–24.
- [13] Roy S, Mandal TN, Barik AK, Pal S, Gupta S, Hazra A, et al. Metal complexes of pyrimidine derived ligands – syntheses, characterization and X-ray crystal structures of Ni(II), Co(III) and Fe(III) complexes of Schiff base ligands derived from S-methyl/S-benzyl dithiocarbazate and 2-S-methylmercapto-6methylpyrimidine-4-carbaldehyde. Polyhedron 2007;26:2603–11.
- [14] Odabaşoğlu M, Albayrak Ç, Özkanca R, Aykan FZ, Lonecke P. Some polyhydroxy azo-azomethine derivatives of salicylaldehyde: synthesis, characterization, spectroscopic, molecular structure and antimicrobial activity studies. | Mol Struct 2007;840:71–89.
- [15] Zhang D, Zhang M, Liu Z, Yu M, Li F, Yi T, et al. Highly selective colorimetric sensor for cysteine and homocysteine based on azo derivatives. Tetrahedron Lett 2006;47:7093-6.
- [16] Ye Z, Boni LD, Neves UM, Mendonça CR, Bu XR. Synthesis and two-photon absorption property of novel salen complexes incorporated with two pendant azo dyes. Tetrahedron Lett 2009;50:1371–3.
- [17] Neves UM, Boni LD, Ye Z, Bu XR, Mendonça CR. Two-photon absorption spectra of salen dye complexes with azo dyes. Chem Phys Lett 2007;441:221–5.
- [18] Geng YY, Gu DH, Gan FX. Spectral and optical recording properties of azo nickel thin film. Mater Sci Eng B 2004;110:115-8.
- [19] Chen ZM, Wu YQ, Gu DH, Gan FX. Nickel(II) and copper(II) complexes containing 2-(2-(5-substitued isoxazol-3-yl)hydrazono)-5,5-dimethylcyclohexane-1,3-dione ligands: synthesis, spectral and thermal characterizations. Dyes Pigment 2008;76:624–31.
- [20] Chen Z, Wu Y, Huang F, Gu DD, Gan FX. Optical properties of nickel(II)–azo complexes thin films for potential application as high-density recordable optical recording media. Solid State Commun 2007;141:1–5.
- [21] Mustroph H, Stollenwerk M, Bressau V. Current developments in optical data storage with organic dyes. Angew Chem Int Ed 2006;45:2016–35.
- [22] Nakai T, Tsukamoto T, Ashida S, Yusu K, Yoshida N, Umezawa K, et al. Duallayer rewritable phase-change recording media for HD DVD system. Jpn J Appl Phys 2004;43:4987–91.
- [23] Khanmohammadi H, Darvishpour M. Copper(II) complexes of pyridazinebased azo-azomethine ligands: synthesis, characterization, thermal and absorption properties. J Inorg Organomet Polym 2011;21:541–6.
- [24] Nejati K, Rezvani Z, Seyedahmadian M. The synthesis, characterization, thermal and optical properties of copper, nickel and vanadyl complexes derived from azo dyes. Dyes Pigment 2009;83:304–11.
- [25] Wei B, Wu YQ, Gu DH, Gan FX. Optical parameters and absorption of azo dye and its metal-substituted compound thin films. Chin Phys Lett 2003;20: 1596–9.
- [26] Huang FX, Wu YQ, Gu DH, Gan FX. Spectroscopy and optical properties of novel metal(II)-azo complex films in blue-violet light region. Chin Phys Lett 2003;20:2259–61.

- [27] Huang FX, Wu YQ, Gu DH, Gan FX. Synthesis, spectroscopic and thermal properties of nickel (II)-azo complexes with blue-violet light wavelength. Dyes Pigment 2005;66:77-82.
- [28] Khanmohammadi H, Darvishpour M. New azo ligands containing azomethine groups in the pyridazine-based chain: synthesis and characterization. Dyes Pigment 2009;81:167–73.
- [29] SMART. Apex II, data collection software, version 2.1. Madison, WI: Bruker AXS Inc.; 2005.
- [30] Bruker. APEX2 version 2009.5-1 and SAINT version 7.34a data collection and processing software. Madison, WI, USA: Bruker Analytical X-Ray Instruments, Inc.; 2009.
- [31] SAINT Plus. Data reduction software, version 7.34a. Madison, WI: Bruker AXS Inc.; 2005.
- [32] Sheldrick GM. SADABS. Göttingen, Germany: University of Göttingen; 2005.
- [33] Sheldrick GM. SHELXS 97, program for crystal structure solution. Göttingen, Germany: University of Göttingen; 1997.
 [34] Sheldrick GM. SHELXL 97, program for crystal structure refinement. Göttin-
- [34] Sneidrick GM. SHELKL 97, program for crystal structure rennement. Gottingen, Germany: University of Göttingen; 1997.
- [35] Densmore CG, Wheeler H, Cohenour R, Robison TW, Hasam D, Cordova BJ, et al. Development of a scaleable synthesis for 1,2-bis(2-aminophenylthio) ethane (APO-link) used in the production of bismaleimide resin. Org Process Res Dev 2007;11:996–1003.
- [36] Yeap G-Y, Heng B-T, Kakeya M, Takeuchi D, Gorecka E, Ito MM. Synthesis, 2D NMR and X-ray diffraction studies on Cu(II) and Ni(II) complexes with ligands derived from azobenzene-cored Schiff base: mesomorphic behaviors of Cu(II)– phenolates and crystal structure of bis[4-(4-alkoxy-2-hydroxybenzylideneamino)azobenzene]copper(II). J Mol Struct 2011;999:68–82.
- [37] Sarkar S, Dey K. Synthesis and spectroscopic characterization of some transition metal complexes of a new hexadentate N₂S₂O₂ Schiff base ligand. Spectrochim Acta A 2005;62:383–93.
- [38] Khanmohammadi H, Abdollahi A. New diaminomaleonitrile-based azo-azomethine dyes; synthesis, characterization and spectral properties. Dyes Pigment 2012;94:163–8.
- [39] Temel H, Pasa S, Ocak YS, Yilmaz I, Demir S, Ozdemir I. Synthesis, characterization, electrochemical behaviors and applications in the Suzuki–Miyaura cross-coupling reactions of N₂S₂O₂ thio Schiff base ligand and its Cu(II), Co(III), Ni(II), Pd(II) complexes and their usage in the fabrication of organic–inorganic hybrid devices. Synth Met 2012;161:2765–75.
- [40] Morshedi M, Amirnasr M, Triki S, Khalaji A. Copper(I) complex [Cu(ca₂₋ dapte)(NCS)] with the flexible N₂S₂ Schiff-base tridentate ligand: synthesis, characterization and crystal structure. J Chem Crystallogr 2011;41: 39–43.
- [41] Acevedo-Chávez R, Costas ME, Escudero R. Allopurinol- and hypoxanthinecopper(II) compounds. Spectral and magnetic studies of novel dinuclear

coordination compounds with bridging hypoxanthine. Inorg Chem 1996;35: 7430–9.

- [42] Bhalla V, Tejpal R, Kumar M, Sethi A. Terphenyl derivatives as "Turn On" fluorescent sensors for mercury. Inorg Chem 2009;48:11677–84.
- [43] Khandar AA, Shaabani B, Belaj F, Bakhtiari A. Synthesis, characterization and spectroscopic and electrochemical studies of new axially coordinated cobalt(III) salen (salen = N, N'-bis(salicylidene)-1,2-ethylenediamine) complexes. The crystal structure of [Co^{III}(salen)(aniline)₂]ClO₄. Polyhedron 2006;25: 1893–900.
- [44] Sanmartín J, García-Deibe Ana M, Bermejo Manuel R, Novio F, Navarro D, Fondo M. Mono- and dinuclear complexes of a flexible Schiff base ligand – crystal structures of a bishelicate and two acentric monohelicates. Eur J Inorg Chem 2003;2003:3905–13.
- [45] Petkova EG, Lampeka RD, Gorichko MV, Domasevitch KV. Nickel(II) and tridentate 8-hydroxyquinoline-2-carbaldehyde-N-methylnitrone (HL): enantioselective association of octahedral [M(HL)(L)]⁺ moieties driven by strong hydrogen bonding. Polyhedron 2001;20:747–53.
- [46] Khandar AA, Cardin C, Hosseini-Yazdi SA, McGrady J, Abedi M, Zarei SA, et al. Nickel(II) and copper(II) complexes of Schiff base ligands containing N₄O₂ and N₄S₂ donors with pyrrole terminal binding groups: synthesis, characterization, X-ray structures, DFT and electrochemical studies. Inorg Chim Acta 2010;363:4080–7.
- [47] Li J, Li X, Wang S. Synthesis, photoluminescent behaviors, and theoretical studies of three novel ketocoumarin derivatives containing an azo moiety. J Mol Struct 2012;1011:19–24.
- [48] Meech SR, Phillips D. Photophysics of some common fluorescence standards. J Photochem 1983;23:193–217.
- [49] Zabulica A, Balan M, Belei D, Sava M, Simionescu B, Marin L. Novel luminescent phenothiazine-based Schiff bases with tuned morphology. Synthesis, structure, photophysical and thermotropic characterization. Dyes Pigment 2013;96:686–98.
- [50] Kharadi GJ. Antitubercular and fluorescence studies of copper(II) complexes with quinolone family member, ciprofloxacin. Spectrochim Acta A 2011;79:898–903.
- [51] Ramachandram B, Samanta A. Transition metal ion induced fluorescence enhancement of 4-(N, N-dimethylethylenediamino)-7-nitrobenz-2-oxa-1,3diazole. J Phys Chem A 1998;102:10579–87.
- [52] Gupta S, Paul BK, Barik AK, Mandal TN, Roy S, Guchhait N, et al. Modulation of fluorescence emission of 1-(2-pyridyl) pyrazole derived Schiff base ligands by exploiting their metal ion sensitive binding modes. Polyhedron 2009;28: 3577–85.
- [53] Majumder A, Rosair GM, Mallick A, Chattopadhyay N, Mitra S. Synthesis, structures and fluorescence of nickel, zinc and cadmium complexes with the N, N, O-tridentate Schiff base N-2-pyridylmethylidene-2-hydroxy-phenylamine. Polyhedron 2006;25:1753–62.