

# Synthesis, spectral and thermal studies of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complex dyes based on hydroxyquinoline moiety

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Received: 15 May 2011 / Accepted: 5 September 2011 / Published online: 24 September 2011  
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**Abstract** A series of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of azo-compounds containing hydroxyl quinoline moiety have been synthesized and characterized by elemental analysis, molar conductance, magnetic moments, IR, electronic and ESR spectral studies. The results revealed the formation of 1:1 and 1:2 (L:M) complexes. The molar conductance data reveal that the chelates are nonelectrolyte. IR spectra indicate that the azodyes behave as monobasic bidentate or dibasic tetradentate ligands through phenolate or carboxy oxygen, azo N for 1:1 (L:M) complexes beside phenolate oxygen and quinoline N atoms for 1:2 (L:M) complexes. The thermal analyses (TG and DTA) as well as the solid electrical conductivity measurements are also studied. The molecular parameters of the ligands and their metal complexes have been calculated.

**Keywords** Azodyes · Complexes · Hydroxy quinoline · Spectral · Thermal · Conductivity

## Introduction

Transition metal azo complexes have played an important role in the development of coordination chemistry [1–17] and have wide applications in industry and biological systems [18–20]. Azo-compounds based on 8-hydroxyquinoline derivatives play a central role as chelating agents for a large number of metal ions [21–24]. Also, some

8-hydroxyquinoline and azo derivatives found numerous applications in analytical chemistry as chromophoric and metallochromic indicators [25–27] as well as Hg<sup>+2</sup> selective chemosensors [28], selective solid phase extraction of trace lead from environmental samples [29]. Recently, thermal analysis techniques play an important role in studying the thermal behavior of metal complexes [30–36].

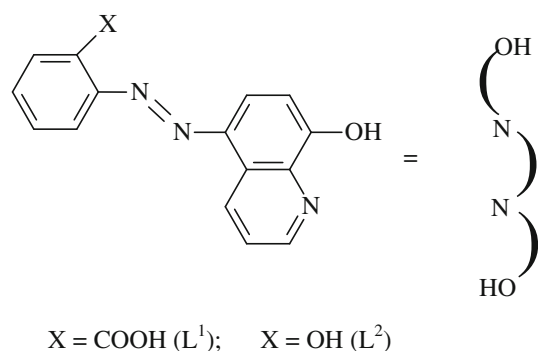
In this study, we described the synthesis and characterization of Mn(II), Co(II), Ni(II) Cu(II) and Zn(II) complexes with azodyes derived from 8-hydroxyquinoline and anthranilic acid or *o*-aminophenol. The interest is focused on study of the chelating properties of these complexes based on elemental analyses, IR, electronic, ESR spectra, molar conductance and magnetic moment measurements. The thermal analysis of the complexes was also used to confirm the structures of the complexes. The electrical conductivity of the Co(II) complex was measured and the activation energy was calculated.

## Experimental

### Preparation of azodyes

All chemicals used were of the highest purity available from BDH. The azodyes used in this investigation (Fig. 1) were prepared by diazotization of *o*-aminophenol or anthranilic acid by dissolving them in HCl, cooling them to 0–5 °C and adding an equivalent amount of ice-cooled sodium nitrite solution with stirring. The cooled diazonium salts were then coupled with 8-hydroxyquinoline. The obtained azodyes were purified by recrystallization from ethanol. The purity of the azodyes was confirmed by elemental analysis, m.p. constancy and by IR spectral studies L<sup>1</sup>: Brown, m.p = 263 °C, analysis: Found, C 62.8; H 4.8;

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**Fig. 1** The structure of azodyes

N 17.4%, Cal. for  $C_{17}H_{16}N_4O_3$ , C 62.96; H 4.93; N 17.28%;  $L^2$ : Orange, m.p. = 165 °C, analysis: Found, C 69.9; H 4.8; N 15.3%, Cal. for  $C_{21}H_{18}N_4O_2$ , C 70.39; H 5.03; N 15.64%; The structures of the prepared azodyes are shown in Fig. 1.

#### Preparation of metal complexes

The metal complexes were prepared by adding stoichiometric quantities (1.0 mmol) of the hydrated metal (II) acetate in 25 mL ethanol to the azodyes (0.5 mmol) in 25 mL ethanol. The mixture was stirred under reflux on a water bath for 1 h, where upon the complexes precipitated on cooling. The resulting solid complexes were filtered off, washed several times with hot ethanol and dried in vacuum desiccator over silica gel. The isolated complexes have m.p. >300 °C and insoluble in most organic solvents, but soluble in DMF. The analytical, spectroscopic and magnetic data as well as the thermal studies enable us to predict the possible structure of the complexes as single crystal cannot be obtained.

#### Physical measurements

Microanalyses (C, H and N) of the solid compounds were carried out on a Heraeus elemental analyzer. Conductometric titrations were performed by titrating the metal ions ( $10^{-4}$  M) with the ligand ( $10^{-3}$  M). Molar conductivities in DMF ( $10^{-3}$  M) at room temperature (25 °C) were measured using Hanna conductometer. The metal contents were complexometrically determined with EDTA after complete digestion in aqua regia and adjusting the pH of the solution to a suitable one. The IR spectra were recorded using Perkin-Elmer spectrophotometer model 1430 covering the range 200–4,000  $cm^{-1}$  using KBr discs. The Nujol mull spectra were determined using Shimadzu UV-Visible 240 spectrophotometer. ESR spectra were recorded by means of JES-FE 2XG (Japan) spectrometer equipped with an E101 microwave bridge. Magnetic moments were

determined on a Johnson Mathey magnetic susceptibility balance. The thermal analysis (TG and DTA) of the solid complexes was performed using Shimadzu TG-50 thermal analyzer in the temperature range up to 800 °C with 10 °C/min heating rate. The electrical conductivity measurements were made on a Super Megohmmeter (Model RM 170) electrometer. The samples were pressed into discs of 13-mm diameter and 1.5–1.6-mm thickness at a pressure  $\sim 700$   $kg\ cm^{-2}$ . The surfaces of the discs were carefully painted with a silver paste. The temperature was measured in air using a Cu/CuNi Comark thermometer placed closed to the sample.

#### Results and discussion

The stoichiometry of the metal complexes of azodyes formed in solution was ascertained by applying the conventional spectrophotometric mole ratio and continuous variation methods [37, 38] as well as by conductometric methods. The results revealed the possible formation of 1:1 and 2:1(M:L) complexes. The results of the elemental analysis (Table 1) indicated the formation of binuclear complexes. The complexes in DMF solutions were found to be nonelectrolyte [39]. This indicates the coordination nature of the acetate ion in complex formation that is confirmed through the addition of  $FeCl_3$  solution to the solution of the solid complexes in which no red brown colour was observed. The relative high values of the conductance suggested the dissociation of the anion through the replacement by DMF solvent.

#### Infrared spectra

The mode of bonding between the azo compound and the titled metal ions was elucidated by examining the IR spectra of the metal complexes in comparison to those of the free azodyes (Table 2). The IR spectra of all complexes exhibited a broad band within the range 3,379–3,553  $cm^{-1}$  assigned to  $\nu_{OH}$  of water or ethanol molecules associated with the complex formation. The  $\nu_{N=N}$  band observed at 1,452 and 1,477  $cm^{-1}$  in the spectra of the free ligands  $L^1$  and  $L^2$ , respectively, was shifted to lower or higher frequency on complex formation, indicating the coordination through the nitrogen atom of the azo group. For the binuclear complexes, the  $\nu_{C=N}$  band of the quinoline ring was shifted to lower or higher wavenumber, indicating that the N-atom of the quinoline ring is involved in complex formation. For mononuclear complexes, the  $\nu_{C=N}$  bands were observed at the same position. The mode of coordination of carboxylate group had been deduced from the magnitude of the observed separation ( $\Delta$ ) between  $\nu_{as}(CO_2)$  and  $\nu_s(CO_2)$ . The separation in complexes was more than 220  $cm^{-1}$

**Table 1** Analytical and physical data of azodye complexes

No.	Complex	Formula	Elemental analysis <sup>a</sup> /%					$\Omega^b$
			C	H	N	M	H <sub>2</sub> O	
1	[Mn <sub>2</sub> L <sup>1</sup> (AcO) <sub>2</sub> (EtOH) <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	C <sub>24</sub> H <sub>31</sub> O <sub>11</sub> N <sub>3</sub> Mn <sub>2</sub>	44.6/43.9	4.8/4.9	6.6/6.5	17.0/16.8	5.6/5.5	17.8
2	[CoL <sup>1</sup> (AcO)(EtOH)(H <sub>2</sub> O) <sub>2</sub> ]	C <sub>20</sub> H <sub>23</sub> O <sub>8</sub> N <sub>3</sub> Co	48.7/48.4	4.6/4.7	8.5/8.4	11.9/11.6	7.3/7.2	31.8
3	[NiL <sup>1</sup> (AcO)(EtOH)](H <sub>2</sub> O)	C <sub>20</sub> H <sub>21</sub> O <sub>7</sub> N <sub>3</sub> Ni	50.6/49.9	4.4/4.5	8.9/8.8	12.3/12.2	3.7/3.4	26.8
4	[Cu <sub>2</sub> L <sup>1</sup> (AcO) <sub>2</sub> (EtOH) <sub>2</sub> ] <sub>3</sub> H <sub>2</sub> O	C <sub>24</sub> H <sub>33</sub> O <sub>12</sub> N <sub>3</sub> Cu <sub>2</sub>	42.2/42.0	4.8/4.6	6.1/5.8	18.6/18.5	7.9/7.5	35.0
5	[Zn <sub>2</sub> L <sup>1</sup> (AcO) <sub>2</sub> (EtOH) <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	C <sub>24</sub> H <sub>29</sub> O <sub>10</sub> N <sub>3</sub> Zn <sub>2</sub>	44.3/43.9	4.4/4.5	6.4/6.4	20.1/19.7	2.7/2.7	40.6
6	[Mn <sub>2</sub> L <sup>2</sup> (AcO) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	C <sub>19</sub> H <sub>23</sub> O <sub>10</sub> N <sub>3</sub> Mn <sub>2</sub>	40.5/40.5	4.0/3.9	7.4/7.5	19.5/19.2	6.3/6.2	–
7	[Co <sub>2</sub> L <sup>2</sup> (AcO)(H <sub>2</sub> O) <sub>3</sub> ] <sub>2</sub> H <sub>2</sub> O	C <sub>17</sub> H <sub>21</sub> O <sub>8</sub> N <sub>3</sub> Co	44.9/44.4	4.6/4.6	9.2/8.9	12.9/12.6	15.8/15.5	33.6
8	[NiL <sup>2</sup> (AcO)(EtOH)](H <sub>2</sub> O)	C <sub>23</sub> H <sub>20</sub> O <sub>6</sub> N <sub>3</sub> Ni	51.2/51.0	4.5/4.5	9.4/8.9	13.2/13.0	4.0/3.9	38.0
9	[CuL <sup>2</sup> (AcO) <sub>2</sub> (EtOH) <sub>2</sub> ](H <sub>2</sub> O)	C <sub>23</sub> H <sub>29</sub> O <sub>9</sub> N <sub>3</sub> Cu <sub>2</sub>	44.6/44.8	4.6/4.2	6.7/6.6	20.5/20.3	2.9/3.0	32.0
10	[ZnL <sup>2</sup> (AcO) <sub>2</sub> (EtOH) <sub>2</sub> ]	C <sub>23</sub> H <sub>27</sub> O <sub>8</sub> N <sub>3</sub> Zn <sub>2</sub>	45.7/45.8	4.5/4.5	7.0/7.0	21.6/21.6	–/–	18.6

<sup>a</sup> (Calc./Found)<sup>b</sup> Ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>**Table 2** IR, electronic spectra and magnetic values of azodyes complexes

Comp.	IR spectra/cm <sup>-1</sup>					$\mu_{\text{eff}}$ BM	Electronic spectra/cm <sup>-1</sup>
	$\nu_{\text{OH}}$	$\nu_{\text{C=N}}$	$\nu_{\text{N=N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$		
L <sup>1</sup>	3,431	1,589	1,511, 1,452	–	–	–	–
1	3,425	1,565	1,498, 1,461	537	471	5.88	19,531, 24,154
2	3,390	1,585	1,579, 1,463	597	508	4.98	15,620, 18,510
3	3,426	1,590	1,498, 1,459	587	475	3.75	14,600
4	3,379	1,575	1,500, 1,461	599	499	1.85	19,263
5	3,404	1,571	1,497, 1,461	549	469	–	–
L <sup>2</sup>	3,304	1,575	1,510, 1,477	–	–	–	–
6	3,432	1,593	1,493, 1,459	587	525	6.01	18,500, 21,700
7	3,553	1,575	1,497, 1,462	514	424	5.00	16,891, 18,939
8	3,410	1,573	1,498, 1,463	590	501	3.68	15,000
9	3,390	1,585	1,497, 1,463	597	508	1.90	17,482
10	3,424	1,585	1,498, 1,461	582	455	–	–

suggesting coordination of carboxylate group in the complexes in a monodentate nature. Also, the  $\nu_{\text{O-H}}$  of the carboxylic group at 2,650 cm<sup>-1</sup> in the free ligand L<sup>1</sup> disappeared in the spectra of the complexes. The new band at 350–400 cm<sup>-1</sup> in the spectra of the complexes is assignable to  $\nu_{\text{M-O}}$ . This supports that the carboxylic group is involved in complex formation. The far infrared spectra of the metal complexes exhibited new bands that are not present in the free ligands. These bands are located at 470–455, 500–490 and 560–530 cm<sup>-1</sup>, assigned to  $\nu_{\text{M-N}}$  of the azo nitrogen,  $\nu_{\text{M-N}}$  of the quinoline ring and  $\nu_{\text{M-O}}$  of the phenolic oxygen, respectively, supporting the bonding of the azo and quinoline nitrogen atoms as well as the phenolic OH group to the metal ions. The absence of  $\delta_{\text{OH}}$  of the free

ligands at 1,320 and 1,330 cm<sup>-1</sup> in the complex formation indicated the deprotonation of OH group. The bands because of  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  of the acetate group are displayed within the ranges 1,520–1,515 and 1,334–1,325 cm<sup>-1</sup>, respectively, in all complexes except Mn(II) complex (6). This affords  $\Delta\nu$  values of 186–190 cm<sup>-1</sup>. Such a frequency separation is characteristic of mono dentate acetate group [40]. The IR spectrum of Mn(II) complex (6) showed two bands at 1,457 and 1,312 cm<sup>-1</sup> assignable to  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  of the acetate group, respectively. The difference between the two bands can be taken as an evidence for the bidentate nature of the acetate group [40]. Also, the IR spectra of the metal complexes exhibited a band within the range 1,170–1,190 cm<sup>-1</sup> assigned to  $\delta_{\text{OH}}$  vibration of bonded C<sub>2</sub>H<sub>5</sub>OH [41]. The IR

spectra of the complexes exhibited bands within the range 730–780  $\text{cm}^{-1}$ . These bands may be assigned to  $\nu_{\text{OH}}$  stretching, rocking and wagging modes of coordination water [40]. According to the IR data, the azodye ligands  $\text{L}^1$  and  $\text{L}^2$  behave as monobasic bidentate and dibasic tetradentate ligands for mono and binuclear complexes, respectively.

#### Electronic spectra and magnetic measurements

The electronic spectral data and the room temperature magnetic moments of the complexes are listed in Table 2.

The electronic spectrum of the tetrahedral Mn(II) complex (**1**) exhibited two bands at 19,531  $\text{cm}^{-1}$  ( ${}^6\text{T}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}(\text{G})$  transition) and 24,154  $\text{cm}^{-1}$  ( ${}^6\text{T}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}(\text{G})$  transition) [42]. The electronic spectrum of octahedral Mn(II) complex (**6**) exhibited two bands at 18,500  $\text{cm}^{-1}$  ( ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}(\text{G})$  transition) and 21,700  $\text{cm}^{-1}$  ( ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}(\text{G})$  transition). The magnetic moment values (6.01 and 5.88 BM for complexes **1** and **6**, respectively) confirmed the aforementioned geometry.

The electronic spectra of the Co(II) complexes showed two bands at 15,620 and 18,510  $\text{cm}^{-1}$  for complex **2**; 16,891 and 18,939  $\text{cm}^{-1}$  for complex **7** assigned to  ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{A}_{2\text{g}}(\text{F})(\nu_2)$  and  ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})(\nu_3)$  transitions, respectively. The magnetic moment values (4.98 and 5.0 BM for complexes **2** and **7**, respectively) are in the range of octahedral Co(II) complexes [43, 44].

The electronic spectra of the tetrahedral Ni(II) complexes exhibited broad bands at 14,600 and 15,000  $\text{cm}^{-1}$  for complexes **3** and **8**, respectively, which can be assigned to  ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ , transition [45]. The magnetic moment values are 3.75 and 3.68 BM, for complexes **3** and **8**, respectively confirmed the aforementioned geometry.

The magnetic moment values of the Cu(II) complexes **4** and **9** are 1.85 and 1.9 BM, respectively. These values indicated that these complexes are monomeric in nature. The electronic spectra of Cu(II) complexes (**4** and **9**) exhibited a broad band with a maximum at 19,267 and 17,482  $\text{cm}^{-1}$  because of the combination of the  ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{E}_{\text{g}}$  and  ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{A}_{1\text{g}}$  transitions in a square planar geometry [46].

#### ESR spectra

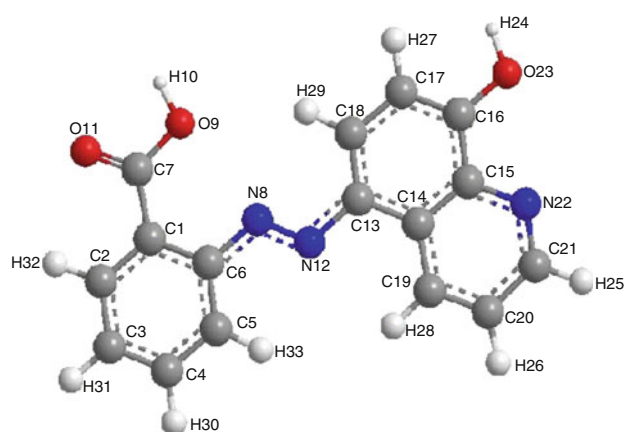
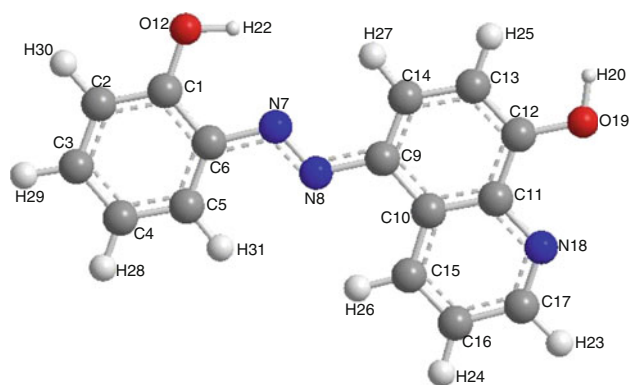
The ESR spectra of the selected solid complexes have been recorded as polycrystalline samples at room temperature (25 °C). The spectra of Cu(II) complexes showed an anisotropic signal with  $g_{\parallel}$  and  $g_{\perp}$  equal to 2.34 or 2.32 and 2.073 or 2.065 for complexes **4** and **9**, respectively. The ordering of  $g$  values ( $g_{\parallel} > g_{\perp} > 2.0023$ ) indicates that the unpaired electron must likely reside in their  $d_{x^2-y^2}$  orbital [47], which is consistent with proposed planar geometry

and  ${}^2\text{B}_{1\text{g}}$  ground state. The splitting of the signal in the high field region may be because of the difference in surroundings between the two Cu(II) centers supporting the binuclear structure for Cu(II) complexes [48]. For Mn(II) complexes **1** and **6**, the ESR spectra of polycrystalline sample give one broad isotropic signal centered at 2.0731 and 2.0112, respectively, i.e., near the free electron value. The broadening of the spectra probably is because of spin relaxation. The  $g$  values are taken to calculate the exchange interaction,  $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$  [49]. If  $G > 4$ , the exchange interaction between Cu(II) centers in the solid state is negligible, whereas when  $G < 4$ , a considerable exchange interaction is indicated. The  $G$  values are 4.7 and 4.92 for complexes **4** and **9**, respectively, suggesting the absence of exchange coupling between Cu(II) centers in the solid state. Furthermore, it has been reported that  $g_{\parallel}$  is 2.4 or 2.3 for Cu–O or Cu–N bonds, respectively [50]. The  $g_{\parallel}$  values for Cu(II) complexes were found larger than 2.3 indicating that the environment is essentially ionic [51].

#### Thermal analysis

From the TG curves, the mass loss was calculated and compared with those theoretically calculated for the suggested formula based on the elemental analyses. The complexes decompose in two steps except complexes **4** and **7**, which decompose in three steps. The first step within the temperature range 25–135 °C brings about a mass loss corresponding to the loss of hydrated (complexes **1**, **3**, **5**, **8** and **9**), coordinated (complexes **2** and **6**) water molecules or ethanol (complex **10**). The second mass loss within the temperature range 150–600 °C may be assigned to complete decomposition of the complexes leading to the metal oxides. The complexes **4** and **7** decompose in three steps corresponding to loss of hydration, coordination water and decomposition of the organic part leading to the metal oxide as final product. There is no further mass loss beyond 600 °C and a plateau is obtained that corresponds to the formation of stable metal oxide from which the metal content was calculated. These values were found in good agreement with the calculated ones for the suggested formula (Table 1).

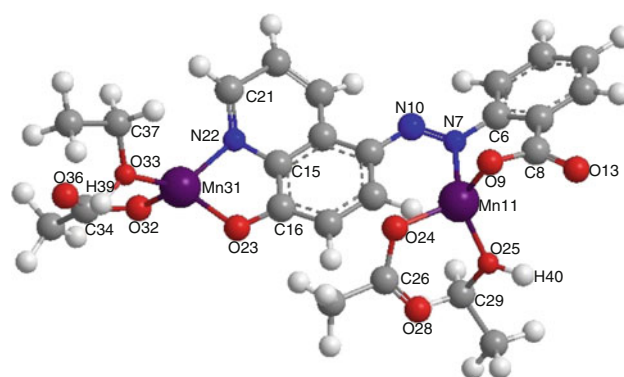
The DTA curve of the complexes (**2**, **4** and **5**) displayed weak endothermic peaks within the temperature range 70–191 °C that are consistent with the loss of hydrated and coordinated water molecules. The broad exothermic peaks lying within the temperature range 203–459 °C included the thermal decomposition of the complexes and loss of the organic portion with the formation of the metal oxide as a final product. The values of the activation energy for the decomposition process were calculated using the method of Piloyan et al. [52]. Arrhenius plots were constructed and the activation energy values were obtained from the slope

L<sup>1</sup>L<sup>2</sup>**Fig. 2** Molecular modeling of L<sup>1</sup> and L<sup>2</sup>

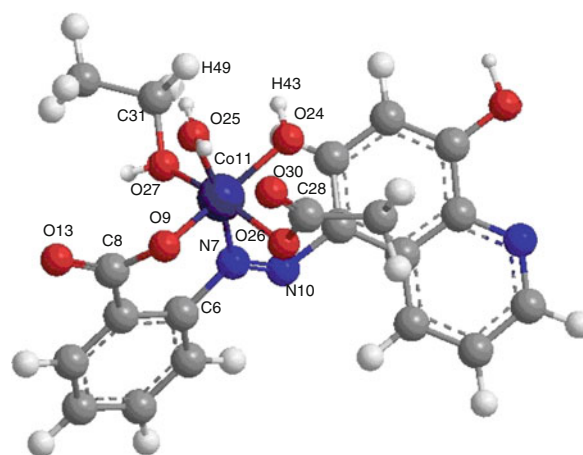
and found to be 26.4, 23.4 and 16.7 kcal/mole for complexes **2**, **4** and **5**, respectively. The values of the activation energies for complexes (**2** and **4**) increase with increasing ionic radii of the metal ion because of the induced electronic delocalization over the whole complex molecule caused from the free OH group.

#### Electrical conductivity measurements

Ligand L<sup>1</sup>, within the temperature range 40–80 °C, exhibited an increase of conductivity as the temperature is increased with activation energy equal 0.851 eV, i.e., an extrinsic behaviour (a positive temperature coefficient). There is a metallic behaviour in the temperature range 80–165 °C with an inflection at 140 °C. The Co(II) complex (**2**) showed a semiconducting behaviour within the temperature range 25–195 °C with phase change at 110 °C. The activation energies  $\Delta E_1$  and  $\Delta E_2$  are 0.047 and 0.148 eV for two regions of semiconductor behaviour of the complex. The conductivity curve of Co(II) complex exhibited a metallic behaviour within the temperature range 195–250 °C.



Complex 1

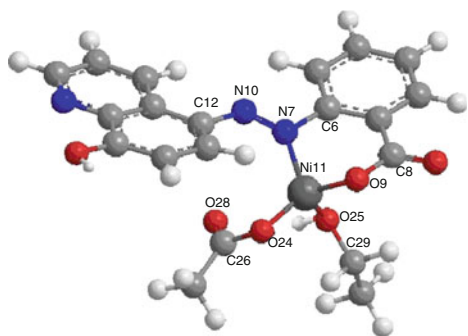


Complex 2

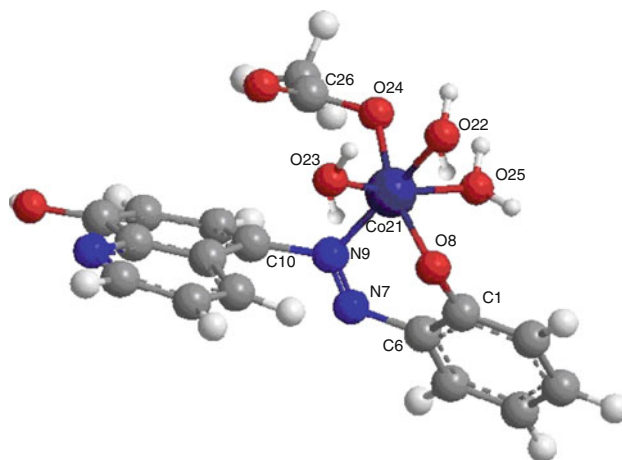
**Fig. 3** Molecular modeling of complexes **1** and **2**

#### Molecular modeling

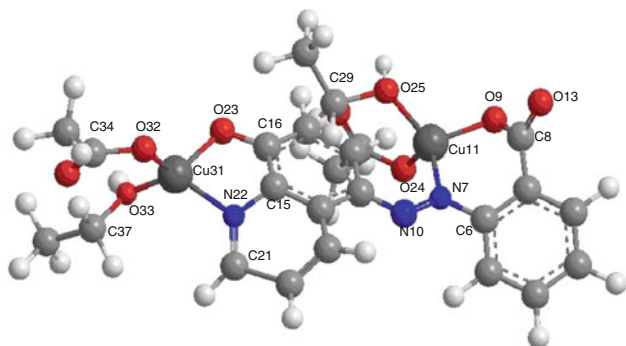
3D molecular modeling of the ligands and their metal complexes was performed using Hyperchem 8.03 molecular modeling. The atomic numbering scheme and the theoretical geometric structures for the ligands L<sup>1</sup> and L<sup>2</sup> and their metal complexes are shown in Figs. 2, 3, 4, 5, 6 and 7. While the main bond lengths are listed in Table 3. For the metal complexes of L<sup>1</sup>, the bond length of the metal–ligand bonds decreased as the ionic radii decreases. In case of binuclear complexes **1**, **4**, **5**, **6** and **9**, it is observed that the bond length of M–N=N, M–O, M–OAc, and M–N quinoline increases in the order Zn(II) > Mn(II) > Cu for L<sup>1</sup> complexes and Mn(II) > Cu(II) for L<sup>2</sup> complexes. For mono nuclear complexes **2**, **3**, **7** and **8**, the bond length increases in the order Co(II) > Ni(II). The lengths of N=N and C=N of quinoline ring are found high in complexes than in the ligand indicating its participation in bonding for binuclear complexes. The length of C=N<sub>quinoline</sub> does not change in 1:1 complexes.



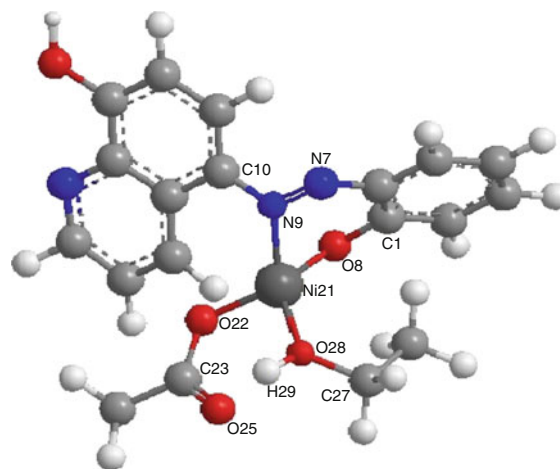
Complex 3



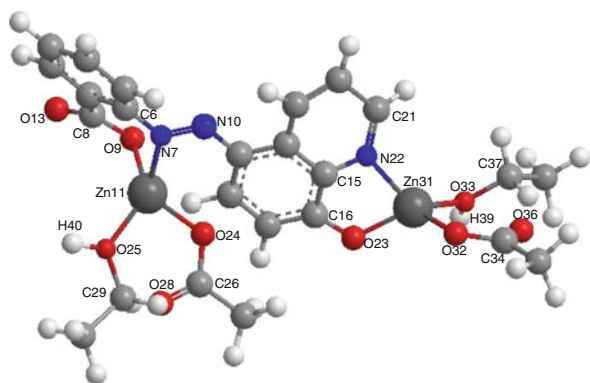
Complex 7



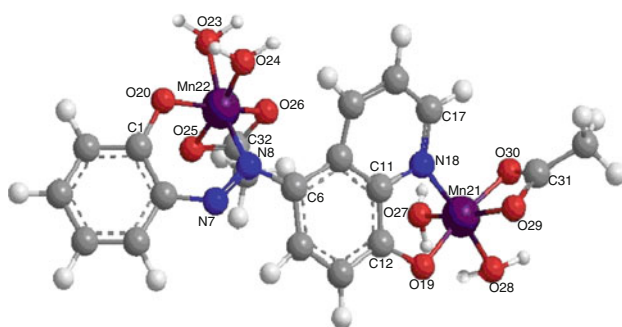
Complex 4



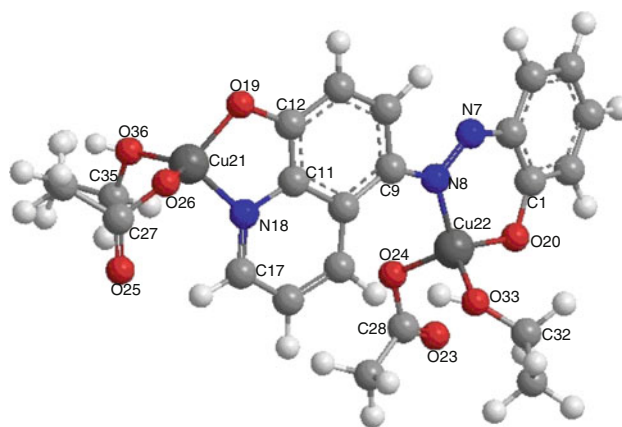
Complex 8

**Fig. 4** Molecular modeling of complexes 3 and 4**Fig. 6** Molecular modeling of complexes 7 and 8

Complex 5

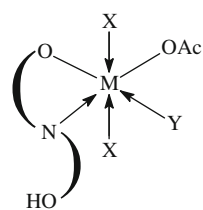


Complex 6

**Fig. 7** Molecular modeling of complex 9**Fig. 5** Molecular modeling of complexes 5 and 6

**Table 3** The bond length of metal complexes of L<sup>1</sup> and L<sup>2</sup>

Comp.	N=N	M–N=N–	M–OHET	M–OAc	M–Opy	M–Oph	M–Npy	M–OCO
L <sup>1</sup>	1.2670	–	–	–	–	–	–	–
1	1.4333	1.8783	1.8349	1.8379	1.8332	–	1.8713	1.8213
2	1.2444	1.8864	1.8314	1.8418	–	–	–	1.829
3	1.2373	1.7929	1.7523	1.7397	–	–	–	1.7474
4	1.2300	1.8539	1.8161	1.8146	1.783	–	1.846	1.7582
5	1.2300	1.9260	1.8900	1.8900	1.7989	–	1.926	1.8876
L <sup>2</sup>	1.2670	–	–	–	–	–	–	–
6	1.3674	1.8901	–	1.8396	1.8300	1.8289	1.8721	–
7	1.2381	1.8794	–	1.83	–	1.8961	–	–
8	1.3123	1.7945	1.7512	1.7388	–	1.7498	–	–
9	1.3608	1.8506	1.8084	1.8042	1.8166	1.8058	1.8479	–
			1.8193	1.8138				

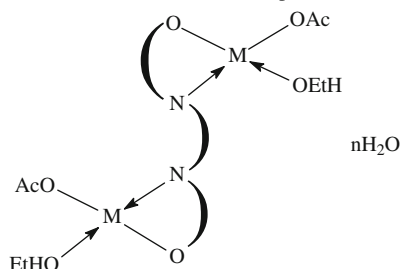


X = H<sub>2</sub>O, Y = EtOH, n = 0 for complex 2

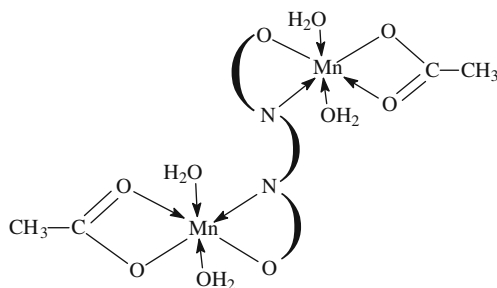
X = 0, Y = EtOH, n = 1 for complex 3

X = Y = H<sub>2</sub>O, n = 1 for complex 7

X = 0, Y = EtOH, n = 1 for complex 8



n = 1 for complexes 5,9; n = 2 for complexes 1, 10; n = 3 for complex 4



Complex 6

**Scheme 1** The structure of the complexes

## Conclusions

Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complex dyes have been synthesised and characterized based on hydroxyl quinoline moiety by combination of elemental analyses, spectral, magnetic, conductance measurements and thermal methods. From the analytical and spectral data, it is concluded that the title azodye acts as monobasic bidentate ligand with azo-nitrogen and phenolic oxygen atoms for 1:1 (M:L) complexes and dibasic tetradentate ligand for 2:1 (M:L) complexes. The spectral and magnetic data revealed the formation of octahedral, tetrahedral or square planar complexes depending on the type of the metal ion. The thermal decomposition of the metal complexes is discussed in relation to structure of the metal complexes. The analytical, spectroscopic and thermal data enable us to predict the possible structures (Scheme 1). The molecular modeling studies supported the geometry around the metal ions (Figs. 2, 3, 4, 5, 6 and 7).

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