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Synthesis and spectroscopic studies of some novel tetra-nuclear metal complexes derived from the reaction of 8,8'-dihydroxy-1,1'-binaphthyl-7,7'-dicarboxylic acid and Co^{III} and Ni^{II} ions

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ABSTRACT

The tetra-nuclear novel solid complexes with the general formulae, $[M_4(H_2L\text{-}2H)Cl_x(H_2O)_y].zH_2O$ ($M = Ni^{II}, Co^{III}$; $x = 6$; $y = 8$; $z = 10$ in case of Ni^{II} ; $x = 10$; $y = 8$; $z = 4$ in case of the Co^{III} complex) and $[Co_2Ni_2(H_2L\text{-}2H)Cl_8(H_2O)_{10}]$, were isolated and characterized by conventional chemical, spectral (IR, UV-Vis., ^{1}H-NMR, Mass), thermal and magnetic measurements. The existence of inter- and intra-molecular hydrogen bonding is confirmed from the results of IR and ^{1}H-NMR spectra. Spectral and magnetic data suggest an octahedral geometry around the metal ions in all isolated metal complexes. The low values of magnetic moments suggest the existence of metal-metal interactions. The amounts of solvents inside and/or outside the coordination sphere were determined by gravimetric analysis.

KEYWORDS

Metal complexes;
8,8'-dihydroxy-1;
1'-binaphthyl-7;
7'-dicarboxylic acid;
Spectral and magnetic studies.

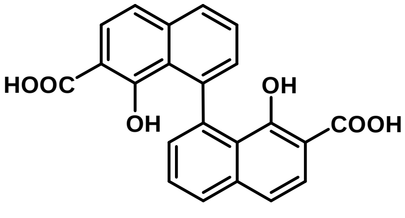
INTRODUCTION

During the past five decades many communications have been reported describing the use of chiral 1,1×-binaphthalene-2,2×-diol (binaphthol) in various aspects, especially in organic synthesis as chirality inducers and catalysts. The development of asymmetric catalysis, in particular for carbon-carbon formation of one of the most challenging and formidable, endeavors in organic chemistry[1,2]. Although 2,2×-disubstituted derivatives of 1,1×-binaphthyl have been used in organic synthesis as chirality inducers[3–6], no work that includes 8,8×-dihydroxy-1,1×- binaphthyl-7,7×-dicarboxylic acid (H_2L) as ligand has been reported earlier. Also, in continuation of our earlier work[7-9] and in view of the importance of this ligand, we report herein the synthesis and characterization of novel tetra-nuclear Ni^{II} and Co^{III} complexes by conventional chemical and physical methods. The possible modes of chelation are discussed on the basis of spectral (UV–vis, IR, ^{1}H NMR, mass) and magnetic measurements. Moreover, thermal measurements (TGA, DTA) have been used to shed more light on the structures of the isolated solid complexes.

EXPERIMENTAL

All the chemicals used were purchased from Fluka and used without purification.

The ligand, 8,8×-dihydroxy-1,1×-binaphthyl-7,7×-dicarboxylic acid (8,8'-DBDA), was prepared by dissolving 3.7g (0.01 mol) of 1-hydroxy-2-naphthoic acid in 500 ml boiling redistilled water. The hot solution was filtered off hot followed by adding $FeCl_3.6H_2O$ (2.7g; 0.01mol) in 10 ml redistilled water. The color of the solution turned grey and intermediate blue precipitate was obtained. The reaction mixture was boiled for 10 min and filtered off. The product obtained was then dissolved in NaOH solution (0.3 N). The iron hydroxide precipitate was removed by filtration and the solution was acidified with dil. HCl (0.2 N). A brown precipitate of the acid (Structure 1) was filtered off, washed firstly with dil. HCl to remove any remaining iron salt followed by redistilled H_2O and finally the brown product was dried in an oven at 120 °C for 2h and then kept in a desiccator over anhydrous $CaCl_2$.



Structure 1

Synthesis of metal complexes

The solid metal complexes were synthesized by adding slowly with a constant stirring a solution of the metal chlorides (2g, mmol) in 25 ml hot absolute EtOH to 2g (2 mmol) of the ligand dissolved in ethanol. The reaction mixture was held under reflux on a hot plate for 3h. The isolated solid complexes were filtered off, washed several times with EtOH and diethyl ether, respectively, and finally kept in a desiccator over $CaCl_2$. All the measurements were carried out as reported earlier[7-9].

RESULTS AND DISCUSSION

The most important IR bands of (8,8×-DBDA) and its metal complexes are depicted in (TABLE 1). The IR spectrum of the ligand (8,8'-DBDA) in KBr shows four bands at 3401, 3374, 3234 and 3060 cm^{-1} assignable to ν(OH) (free naphthyl), ν(OH) (free carboxylic) ν(OH) (carboxylic hydrogen-bonded)[10] and ν(OH) (naphthyl hydrogen-bonded) vibrations, respectively. The observation of the former band as a medium one while the negative shift of the second band to lower wave-number suggests that the ligand exists in equilibrium between the free and the hydrogen-bonded forms Meanwhile, the position of the third and the fourth bands indicates that two molecules of (8,8'-DBDA) are linked together through inter-molecular hydrogen bonding as shown in (Structure 2).

This assumption is proposed on the basis of the following evidence. Several broad but weak bands are observed in the 2700-2500 and 2000-1800 cm^{-1} regions indicating the presence of hydrogen bonding of the type O—H……..O[11-14] which may be inter- or intra-molecular hydrogen bonding.

The ^{1}H-NMR spectrum of (8,8'-DBDA)

The position of δ(OH) carboxylic acid in the ^{1}H-NMR spectrum of the ligand (8.8'-DBDA) in d_6-DMSO is observed at 12.6 ppm, in respect of TMS. In contrast, the position of δ(OH; naphthyl) is observed at 10.21 ppm. This supports the existence of intra-molecular hydrogen bonding between the two naphthyl OH groups. Both the signals disappear upon deuteration. Also, the multiple signals are observed in the 7-8.8 ppm range assigning to the protons of phenyl rings.

Mass spectrum of (8,8'-DBDA)

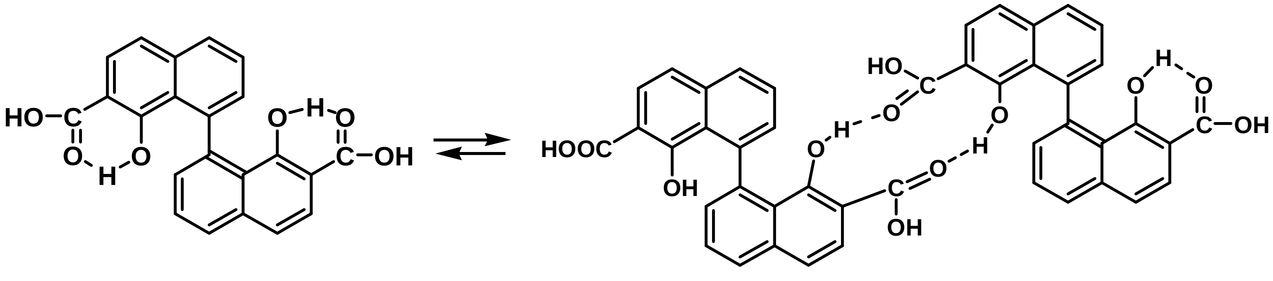
The mass spectrum of the ligand shows the molecular ion peak ion at 383. This suggests that the proposed structure for the ligand is matched with the chemical formula; $C_{22}H_{14}O_6.1/2H_2O$; M.wt. = 383.3. The existence of $1/2H_2O$ is confirmed from the elemental analyses and the mass spectrum of the compound. Also, the band observed at 3606 cm^{-1} in the IR spectrum of the ligand can be taken as evidence for the existence of water within the formula. The fragmentation pattern of the ligand is represented in (Scheme 1).

Moreover, the observation of two bands in the IR spectrum at 1686 and 1623 cm^{-1}, assignable to the free and hydrogen bonded carbonyl oxygen, respectively, is taken as additional evidence for the presence of intra-molecular and inter-molecular hydrogen bonding (Structure 2).

TABLE 1 : The most important IR spectral bands for the ligand and its metal complexes

Compound	ν (OH)	ν_a (C=O)	ν_s (C=O)	ν (C-O)	$^a\Delta$	δ(OH) Phenolic, crboxylic	ν (M-O)
$C_{22}H_{14}O_6$+1/2H_2O (8.8'-DBDA)	3419, 3374	1714	1623	1363, 1236	-	1157, 1236	
[$Ni_4(H_2L$-2H)$Cl_6(H_2O)_8$].10H_2O	3444, 3416	1637	1423	1348	75	1119	474
[$Co_4(H_2L$-2H)]$Cl_{10}(H_2O)_8$].4H_2O	3444, 3416	1619	1424	1349	75	1069	420, 475
[Co_2,$Ni_2(H_2L$-2H)$Cl_8(H_2O)_{10}$]	3444, 3416	1618	1422	1348	74	1069	445, 528

[a] **difference between $\nu_{a\ \text{and}}\ \nu_s$**



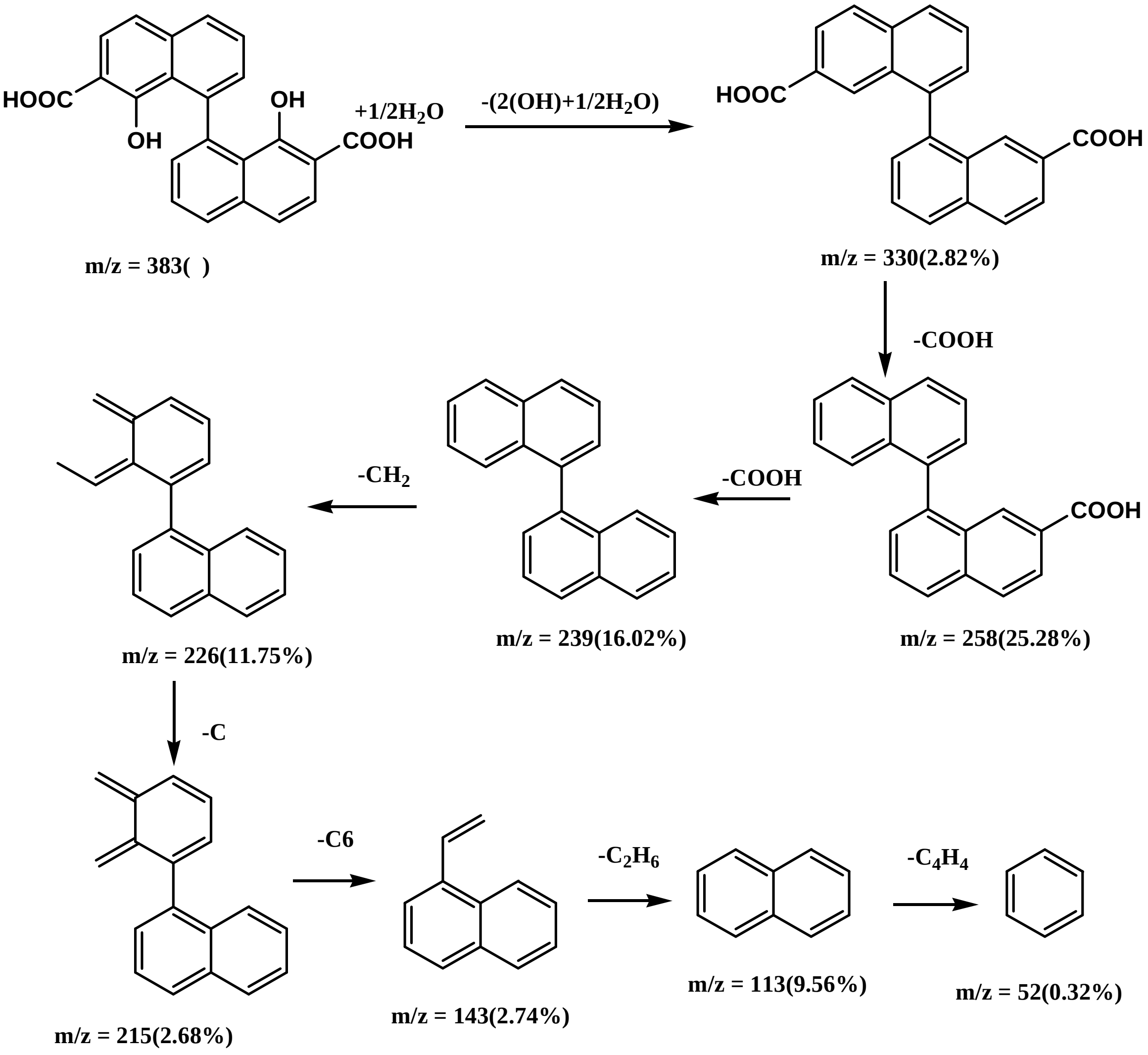
Structure 2

It is worthy to infer that the intra-molecular hydrogen bonding is much stronger than that of the inter-molecular one due to the size of the ring formed[15]. The formation of a chelate ring with a six-member ring between the OH naphthyl and carbonyl oxygen is responsible for the stability of the intra-molecular hydrogen bonding in comparison to the inter-molecular one. The observation of four bands at 1282, 1236, 1070 and 1014 cm^{-1} assignable to ν(C-O) (carboxylic), ν(C-O) (naphthyl), δOH naphthyl) and δOH (carboxylic) vibrations[14], respectively, suggests the symmetry of functional groups around the ring formed in the ligand (8,8-DBDA). On comparing the IR spectra of the free ligand with its metal complexes, one observes that the free ligand behaves in a bidentate manner *via* the carboxylic (COOH) group forming four-member ring as in case of all metals and through the OH (naphthyl) and OH (carboxylic) groups without displacement of proton from each group forming six-member ring around the metal ion and with displacement of proton forming six-member ring.

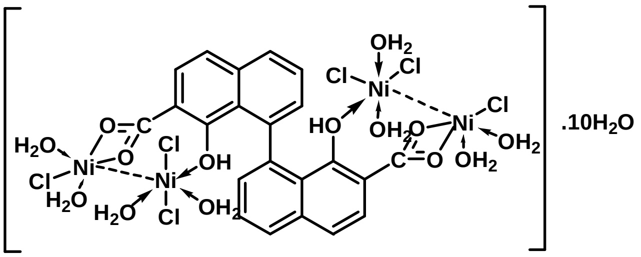
Firstly, the ligand (8,8'-DBDA) coordinates to four Ni^{II} ions, with a ratio 4:1 (M:L), *via* the carboxylic (COOH) group with displacement of a hydrogen atom forming four-member ring around Ni^{II} ions as shown in (Structure 3).

This behavior is supported by the following evidence. The ν(C=O) vibration band disappears together with the appearance of two new bands at 1637 and 1423 cm^{-1} assigned to $\nu_a(COO^-)$ and $\nu_s(COO^-)$ vibrations[16], respectively. The difference between these two bands, $\nu_s(COO^-)$ and ν(C-O) vibrations, (75 cm^{-1})[16] suggests that the bond between the nickel and oxygen atoms[17], is very strong as well as the stability of the isolated Ni^{II} complex. Also, this explains the high melting point of the Ni^{II} complex as well as the coordination of the carboxylate group in a bidentate manner. This behavior is also observed for the other metal complexes isolated from the ligand under investigation (8,8'-DBDA). The δ(OH) (carboxylic, out-of plane) at 1157 cm^{-1}[10] disappears while the intensity of the δ(OH) (naphthyl) at 1119 cm^{-1} decreases and shifted to higher wave-number, in comparison to its position of the free ligand (1236 cm^{-1}), due to hydrogen bonding. This is mainly due to the overlapping of the δ(OH) vibration of both water of hydration and coordination. Finally, a new band appears at 474 cm^{-1} assignable to ν(Ni-O) vibrations[18]. All these foundations together with the results of elemental analyses (TABLE 2) suggest that the chemical formula of the Ni^{II} complex is [$Ni_4(H_2L$-2H)$Cl_6(H_2O)_8$].10H_2O.

The electronic spectrum of the Ni^{II} complex, [$Ni_4(H_2L$-2H)$Cl_6(H_2O)_8$].10H_2O, shows bands at 27855, 17986 and 12870 cm^{-1} attributed to ν_3, ν_2 and ν_1 vibrations, respectively, in an octahedral geometry around the two symmetric Ni^{II} ions. The ligand field parameters are calculated and found to be 482 and 0.47 for B and β, respectively. On the other hand, the



Scheme 1



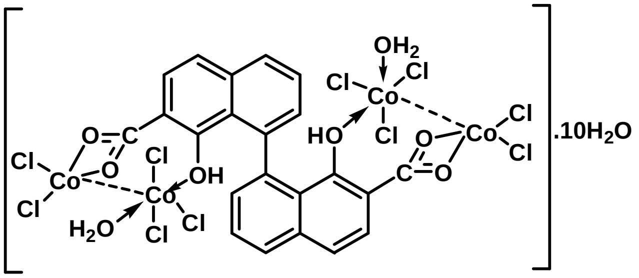
Structure 3

electronic spectrum of the other two symmetric Ni^{II} ions attached to the hydroxyl groups shows three bands at 34483, 23696 and 14388 cm^{-1} assigned to ν_3, ν_2 and ν_1 vibrations, respectively, in an octahedral geometry around the other two Ni^{II} ions. The ligand field parameters are calculated and found to be 1001 cm^{-1} and 0.97 for B and β, respectively. The low values of β in the previous case suggest that the bond between the carboxylate groups and the Ni^{II} ions are mainly covalent nature. In contrarily the high values in case of the other two Ni^{II} ions indicate that the bond between the hydroxyl and the Ni^{II} ions are mainly ionic in nature.

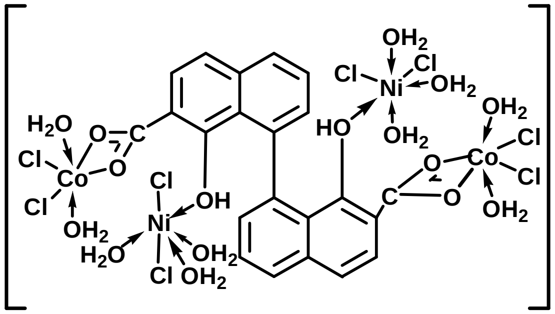
Also, the ligand coordinates to four Co^{II} ions, with a ratio 4:1 (M:L), coordinating *via* the carboxylic group(COOH) with displacement of a hydrogen atom forming four-member ring around Co^{II} ions as shown in (Structure 4).

This behavior is supported by the following evidence. The ν(C=O) stretching band disappears together with the appearance of two new bands at 1619 and 1424cm^{-1} assigned to $\nu_a(COO^-)$ and $\nu_s(COO^-)$ vibrations[16], respectively. The difference between these two bands, $\nu_s(COO^-)$ and ν(C-O) vibrations, (75 cm^{-1})[16] suggests that the bond between cobalt and oxygen[17] is very strong as well as the stability of the isolated the Co^{III} complex. Also, this explains the high melting point of the Co^{III} complex as well as the coordination of the acetate group in a bidentate manner. This behavior is also observed for the other metal complexes isolated from the ligand (8,8'-DBDA). The δ(OH) (carboxylic, out-of plane[10] at 1157 cm^{-1} disappears while the intensity of the δ(OH) (naphthyl) at 1069 cm^{-1} decreases and shifted to higher wave-number, in comparison to its position of the free ligand (1236 cm^{-1}), due to hydrogen bonding. This is mainly due to the overlapping of the δ(OH) vibration of both water of hydration and coordination. Finally, a new band appears at 420, 475 cm^{-1} assignable to ν(Co-O) vibration[18]. All these foundations together with the results of the elementals analyses (TABLE 2) suggest that the chemical formula of the Co^{II} complex is $[Co_4(H_2L\text{-}2H)]Cl_{10}(H_2O)_8].4H_2O$. The electronic spectrum of this complex shows bands at 29498, 25380 and 13531 cm^{-1} attributed to ν_3, ν_2 and ν_1 vibrations, respectively, in an octahedral geometry around the two symmetric Co^{III} ions attached to the hydroxyl groups. The ligand field parameters are calculated and found to be 952 and 0.86 for B and β, respectively. On the other hand, the electronic spectrum of the other two symmetric Co^{III} ions attached to the carboxylate groups shows three bands at 16051, 514 and 923 cm^{-1} assigned to ν_3, ν_2 and ν_1 vibrations, respectively, in a tetrahedral geometry around the other two Co^{III} ions[19]. The ligand field parameters are calculated and found to be 1028 cm^{-1} and 0.96 for B and β, respectively. The high value of β in the previous case suggests that the bond between the hydroxyl groups and the two Co^{III} ions is mainly ionic nature. In addition to the high value in case of the other two Co^{III} ions indicates that the bond between the carboxylate and the Co^{III} ions is mainly ionic in nature.

Four Co^{II} and Ni^{II} ions, with a ratio 2:2:1 (M:M:L), *via* the carboxylic (COOH) group without displacement of a hydrogen atom forming four-member ring around Co^{II} and Ni^{II} ions as shown in (Structure 5).



Structure 4



Structure 5

This behavior is supported by the following evidence. The ν(C=O) band disappears together with the appearance of two new bands at 1618 and 1422 cm^{-1} (Figure) assigned to $\nu_a(COO^-)$ and $\nu_s(COO^-)$ vibrations[16], respectively. The difference between these two bands $\nu_s(COO^-)$ and ν(C-O) vibrations (75 cm^{-1})[16] suggests that the bond between nickel, cobalt and oxygen[16] is very strong as well as the stability of the isolated Ni^{II} and Co^{III} complex. Also, this explains the high melting point of the complex as well as the coordination of the acetate group in a bidentate manner. This behavior is also observed for the other metal complexes isolated from the ligand (8,8'-DBDA). The δ(OH)(carboxylic, out-of plane [117] at 1157 cm^{-1} disappears while the intensity of the δ(OH) (naphthyl) at 1069 cm^{-1} decreases and shifted to higher wave-number in comparison to its position of the free ligand (1236 cm^{-1}), due to hydrogen bonding. This is mainly due to the overlapping of the δ(OH) vibration of both water of hydration and coordination. Finally, a new band appears at 528 and 445 cm^{-1} assignable to ν(Co-O) and ν(Ni-O) vibrations[18], respectively. All these foundations together with the results of the elementals analyses (TABLE 2) suggest that the chemical formula of the Co^{II} and Ni^{II} complexes is $[Co_2,Ni_2(H_2L\text{-}2H)Cl_8(H_2O)_{10}]$.

The electronic spectrum of the mixed complex containing both the Co^{III} and Ni^{II} ions, $[Co_2,Ni_2(H_2L\text{-}2H)Cl_8(H_2O)_{10}]$, shows three bands at 28571, 20576 and 14025 cm^{-1} attributed to ν_3, ν_2 and ν_1 vibrations, respectively, in an octahedral geometry around the two symmetric Co^{III} ions attached to the carboxylate groups. The ligand field parameters are calculated and

TABLE 2. Elemental analyses and some physical data of the metal complex.

Compound	M. Wt.	Color	M.p.; °C	% Found (Cald.)				$\mu_{eff.}$, B.M.
				C	H	M	Cl	
$C_{22}H_{14}O_6$+1/2H_2O (8.8'-DBDA)	383.3	White	210	67.65 (68.99)	5.46 (4.21)	-	-	-
$[Ni_4(H_2L\text{-}2H)Cl_6(H_2O)_8].10H_2O$	1144.18	Dirty white	>300	(23.09)	3.75 (4.20)	21.20 (20.50)	17.60 (18.60)	2.17
$[Co_4(H_2L\text{-}2H)]Cl_{10}(H_2O)_8].4H_2O$	1178.78	Pale pink	>300	(22.42)	3.20 (3.10)	18.94 (20.00)	30.10 (30.00)	8.09
$[Co_2,Ni_2(H_2L\text{-}2H)Cl_8(H_2O)_{10}]$	1071.40	Dirty white	>300	(24.66)	2.28 (3.00)	Co, 10.90(11.00) Ni, 10.20(10.90)	25.95 (26.50)	3.94

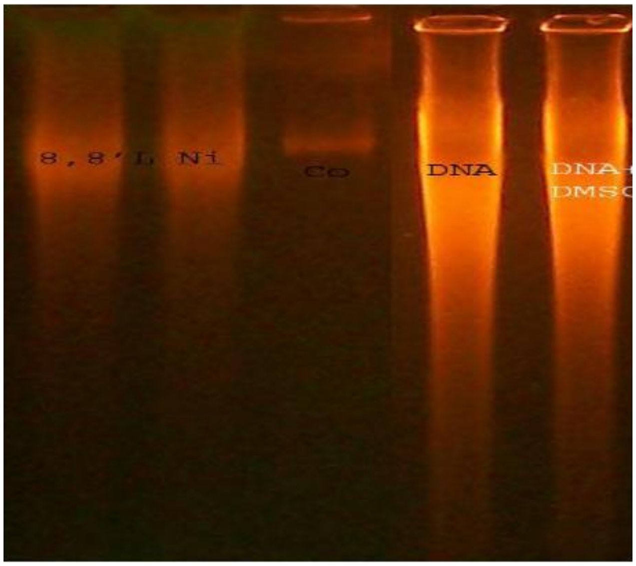


Figure1: Biological effects of the ligand and its metal complexes on Calf-Thymus (DNA).

found to be 471 and 0.44 for B and β, respectively. On the other hand, the electronic spectrum of the other two symmetric Ni^{II} ions attached to the hydroxyl groups shows three bands at 24752, 17301and 12953 cm^{-1} assigned to ν_3, ν_2 and ν_1 vibrations, respectively, in an octahedral geometry around the other Ni^{II} ions. The ligand field parameters are calculated and found to be 212 cm^{-1} and 0.2 for B and β, respectively. The low values of β in the complex suggest that the bond is mainly covalent nature.

DNA studies

The effects of the genotoxicity on the DNA for the 8,8'-dihydroxy-1,1'-binaphthyl-7,7'-dicarboxylic acid (8,8'-DBDA) and their metal complexes of Ni^{II} and Co^{III} ions with the formulae, $[Ni_4(H_2L\text{-}2H)Cl_6(H_2O)_8].10H_2O$ and $[Co_4(H_2L\text{-}_2H)]Cl_{10}(H_2O)_8].4H_2O$, in comparison to the control sample indicate an interesting results. The degradation power of the tested ligand on Calf-Thymus DNA is high as for the complexes supporting the selective action of the ligand against human or related eukaryotic organisms. Also, the results suggest that a direct contact of the ligand and its Ni^{II} and Co^{III} complexes are necessary to degrade the DNA of eukaryotic subject[20]. The results give promising results to use the 8,8'-dihydroxy-1,1'-binaphthyl-7,7'-dicarboxylic acid (8,8'-DBDA) and its complexes as anti-tumor.

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