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### Spectroscopic Characterization of Oxime Ligands and Their Complexes

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## Spectroscopic Characterization of Oxime Ligands and Their Complexes

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### ABSTRACT

New imine–oxime ligands  $H_3L^1$ – $H_3L^3$  have been obtained from reactions of the Schiff base ligands  $H_2B^1$ – $H_2B^3$  with monochloroglyoxime. Mononuclear copper(II), cobalt(II), nickel(II), vanadyl(IV) and zinc(II) complexes of the imine–oxime ligands  $H_3L^1$ – $H_3L^3$  have been prepared and characterized by elemental analyses, infrared and electronic spectra, magnetic moment and molar conductance data. The molar conductance data show that the complexes are non-electrolytes. When the imine–oxime ligands react with the metal salts in a 2:1 ratio, they behave as dibasic bidentate ligands towards one metal ion. The nickel(II) and zinc(II) complexes are diamagnetic. The  $^1H(^{13}C)$ -nmr spectra of all

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ligands and nickel(II) and zinc(II) complexes of the ligands  $H_3L^1$ – $H_3L^3$  have been recorded. Mass spectra of the imine–oxime ligands and their nickel(II) and zinc(II) complexes were recorded. Some of the ligands and metal complexes have antibacterial activity.

**Key Words:** Oxime; Complex; Antibacterial.

## INTRODUCTION

Oximes and their metal complexes are of current interest for their rich physicochemical properties, reactivity patterns and potential applications in many important chemical processes in the areas of medicine,<sup>[1,2]</sup> bioorganic systems,<sup>[3,4]</sup> catalysis,<sup>[5,6]</sup> electrochemical and electrooptical sensors.<sup>[7]</sup> The high stability of the complexes prepared with *vic*-dioxime ligands has been extensively used for various purposes including model compounds for vitamin B<sub>12</sub> or trace metal analysis.<sup>[8]</sup> The successful design and synthesis of ligands capable of forming heteronuclear complexes has been receiving attention for their magnetic, optical and electrical properties.<sup>[9,10]</sup> Examples of heteronucleating ligands, which could serve as polytopic receptor molecules for the binding or cobinding of metal ions and molecular substrates include molecules that contain various functionalities appended to porphyrins, phthalocyanines, salen centers and macro cyclic tetra amines.<sup>[11,12]</sup> The presence of weakly acidic hydroxyl groups and slightly basic nitrogen atoms make vicinal dioxime amphoteric ligands that form corrin-type square-planar, square-pyramidal and octahedral complexes with transition metals such as nickel(II), copper(II), palladium(II) and cobalt(II) as central atoms.<sup>[13,14]</sup> The ability of oxime-containing ligands to stabilize reduced and oxidized forms of metal ions has importance in technological applications. Schiff bases and oxime compounds have been extensively studied because of their biological and structural importance<sup>[15]</sup> arising from their specific and selective reactions with metal ions.

The aim of this work is the synthesis and characterization of the imine–oxime ligands and their Cu(II), Co(II), Ni(II), Zn(II), VO(IV) metal complexes.

## EXPERIMENTAL

### Materials

All solvents and metal salts used for the synthesis and physical measurements were purchased in their highest commercial purity, and were used



without further purification. The compounds 4-Nitrobenzaldehyde, 4-aminothiophenol, salicylaldehyde, *o*-vanillin, 5-bromosalicylaldehyde, Pd/C (10%) and N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O (100%) were used as supplied by Fluka. Monochloroglyoxime was synthesized according to a published method.<sup>[16]</sup>

### Physical Measurements

Elemental analyses (C, H, N, S) were performed using a Leco 932 elemental analyser. IR spectra were obtained using KBr discs (4000–400 cm<sup>-1</sup>) on a Shimadzu 8300 FT-IR spectrophotometer. The electronic spectra in the 200–900 nm range were obtained on a Shimadzu UV-160 A spectrophotometer. Magnetic measurements were carried out by the Gouy method using Hg[Co(SCN)<sub>4</sub>] as calibrant. Molar conductances of the imine–oxime ligands H<sub>3</sub>L<sup>1</sup>–H<sub>3</sub>L<sup>3</sup> and their transition metal complexes were determined in DMSO ( $\sim$ 10<sup>-3</sup> M) at room temperature using a Jenway Model 4070 conductivity meter. The mass spectra analyses were carried out on a Micromass, UK, platform II, LC-MS spectrophotometer. Electrospray ionization (ESI) mass spectra were obtained using a methanol:acetic acid (50:50) mobile phase. The methanol:acetic acid mixture were directly injected into a API-II (Atmospheric pressure ionization for MS 700T) attached to the spectrometer. A Harvard pump II was used to deliver the solution to the API-II at a flow rate of 50 cm<sup>3</sup> min<sup>-1</sup>. Pressure in the mass analyzer region was usually about 5  $\times$  10<sup>-3</sup> Pa. <sup>1</sup>H–, and <sup>13</sup>C-n.m.r. spectra were recorded on a Varian XL-200 instrument. TMS was used as internal standard and deuterated DMSO as solvent. The metal contents of the complexes were determined by use of an ATI Unicam 929 Model AA Spectrometer in solutions prepared by decomposing the compounds in aqua regia and subsequently by digestion in concentrated hydrochloric acid.

### Schiff Base Ligand (A)

The Schiff base ligand A was prepared by condensing 4-nitrobenzaldehyde (1 mmol, 0.168 g) with the 4-aminothiophenol (1 mmol, 0.142 g) in EtOH (40 cm<sup>3</sup>) by boiling the mixture under reflux for 5–6 h. The precipitated ligand was filtered, recrystallized from Me<sub>2</sub>CO/C<sub>6</sub>H<sub>12</sub> (v/v) and dried in a *vacuum* desiccator.

**A:** Yield: 0.25 g (90%), yellow crystals, m.p. 119–121°C. Electronic spectrum (EtOH,  $\lambda_{\text{max}}$ /nm): 356, 350, 318, 281, 205. FT-IR (KBr, cm<sup>-1</sup>): 2567 (Ar–SH), 1633 (C=N), 1516, 1492 (NO<sub>2</sub>). <sup>1</sup>H-n.m.r. (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 8.40 (1H, s, CH=N), 6.18–7.35 (8H, m, Ar–H), 3.50 (1H, s, SH). <sup>13</sup>C-n.m.r. (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 162.5 (CH=N), 110.15–



157.50 (Ar-C). (Found: C, 60.49; H, 3.90; N, 10.89; S, 12.35 %.  $C_{13}H_{10}N_2O_2S$  calcd.: C, 60.46; H, 3.87; N, 10.85; S, 12.40%).

### Amine Compound (B)

The compound A (2 mmol, 0.516 g) was dissolved in EtOH (100 cm<sup>3</sup>) and the solution was heated to 80°C. Pd/C (10%) (0.70 g) was then added to this solution at the same temperature and 20 cm<sup>3</sup> of hydrazine hydrate (100%) was added dropwise. The mixture was stirred and refluxed for 50 min. After cooling to room temperature, the mixture was filtered. The dirty orange product was extracted with chloroform. The volume of the extract was reduced under *vacuum* and cooled in a refrigerator at -10°C. The formed crystals were filtered and washed with cold hexane.

**B:** Yield: 0.46 g (80%), orange crystals, m.p. 218°C. Electronic spectrum (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ): 351, 316, 251, 218. FT-IR (KBr, cm<sup>-1</sup>): 3356 (NH<sub>2</sub>), 3213 (NH), 2922 (CH<sub>2</sub>). <sup>1</sup>H-n.m.r. (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 6.53–7.14 (8H, m, Ar-H), 4.40 (1H, t, NH), 4.15 (2H, d, CH<sub>2</sub>), 3.35 (1H, s, SH). <sup>13</sup>C-n.m.r. (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 114.28–150.81 (Ar-C), 48.40 (CH<sub>2</sub>). Analysis: found: C, 67.80; H, 6.11; N, 12.13; S, 13.94%. Calculated for  $C_{13}H_{14}N_2S$ : C, 67.83; H, 6.09; N, 12.17; S, 13.91%.

### Preparation of the Ligands $H_2B^1$ – $H_2B^3$

To a stirred solution of the amine compound (2 mmol, 0.460 g) in 20 cm<sup>3</sup> of absolute ethanol/chloroform (1:1 by volume) mixture were added to the carbonyl derivatives in 10 cm<sup>3</sup> of absolute ethanol. The resulting mixture was heated at reflux for 2 h and the solvent was evaporated in *vacuo*. The resulting products were washed with cold ethanol, and dried under *vacuum* dessicator.

**$H_2B^1$ :** Yield: 0.39 g (90%), orange crystals, m.p. 151°C. Electronic spectrum (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ): 360, 349, 295, 237, 214. FT-IR (KBr, cm<sup>-1</sup>): 3425 (OH), 2933 (CH<sub>2</sub>), 2644 (Ar-SH), 1640 (C=N). <sup>1</sup>H-n.m.r. (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 10.35 (1H, s, OH), 8.63 (1H, s, CH=N), 6.21–7.72 (12H, m, Ar-H), 5.34 (1H, t, NH), 3.35 (2H, s, SH), 2.52 (2H, s, CH<sub>2</sub>). <sup>13</sup>C-n.m.r. (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 160.54 (CH=N), 113.14–157.40 (Ar-C), 60.46 (CH<sub>2</sub>). (Found: C, 71.89; H, 5.41; N, 8.35; S, 9.61 %.  $C_{20}H_{18}N_2OS$  calcd.: C, 71.86; H, 5.39; N, 8.38; S, 9.58%).

**$H_2B^2$ :** Yield: 0.42 g (87%), orange crystals, m.p. 129°C. Electronic spectrum (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ): 367, 349, 307, 210. FT-IR (KBr, cm<sup>-1</sup>): 3444 (OH), 2929 (CH<sub>2</sub>), 2597 (Ar-SH), 1640 (C=N). <sup>1</sup>H-n.m.r. (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 10.57 (1H, s, OH), 8.40 (1H, s, CH=N), 6.18–7.50 (11H, m, Ar-H), 5.57 (1H, t, NH), 4.12 (3H, s, OMe), 3.34 (2H, s, SH), 2.43 (2H,

s,  $\text{CH}_2$ ).  $^{13}\text{C}$  n.m.r. (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 161.68 (CH=N), 112.33–155.72 (Ar-C), 61.15 (CH<sub>2</sub>), 56.77 (OMe). (Found: C, 69.19; H, 5.47; N, 7.73; S, 8.75 %.  $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$  calcd.: C, 69.23; H, 5.50; N, 7.69; S, 8.79%).

**H<sub>2</sub>B<sup>3</sup>:** Yield: 0.36 g (88%), dark yellow crystals, m.p. 217°C. Electronic spectrum (EtOH,  $\lambda_{\text{max}}$ /nm): 368, 339, 301, 249, 214. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3445 (OH), 2921 (CH<sub>2</sub>), 2366 (Ar-SH), 1637 (C=N).  $^1\text{H}$ -n.m.r. (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 11.48 (1H, s, OH), 8.56 (1H, s, CH=N), 6.20–7.67 (12H, m, Ar-H), 5.54 (1H, t, NH), 3.56 (2H, s, SH), 2.68 (2H, s, CH<sub>2</sub>).  $^{13}\text{C}$ -n.m.r. (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 162.17 (CH=N), 113.72–154.24 (Ar-C), 61.40 (CH<sub>2</sub>). (Found: C, 58.09; H, 4.16; N, 6.82; S, 7.79 %.  $\text{C}_{20}\text{H}_{17}\text{N}_2\text{OSBr}$  calcd.: C, 58.11; H, 4.12; N, 6.78; S, 7.75%).

### Preparation of *vic*-Dioximes

The new *vic*-dioxime ligands ( $\text{H}_3\text{L}^n$ , n: 1, 2 or 3) were prepared according to the procedure below. A solution of monochloroglyoxime in dichloromethane (25 cm<sup>3</sup>), which was prepared from glyoxime (5 mmol, 0.785 g) and an aqueous solution of  $\text{Na}_2\text{CO}_3$  (25 cm<sup>3</sup>), was added with stirring to a solution of the ligands H<sub>2</sub>B<sup>n</sup> [5.0 mmol, 1.670 g for H<sub>2</sub>B<sup>1</sup>, 1.820 g for H<sub>2</sub>B<sup>2</sup> and 2.065 g for H<sub>2</sub>B<sup>3</sup>] in  $\text{CH}_2\text{Cl}_2$  (80 cm<sup>3</sup>) at room temperature. The reaction was continued for 10 h at 40°C temperature and the resulting compound was separated by filtration, washed with cold  $\text{CH}_2\text{Cl}_2$  and  $(\text{C}_2\text{H}_5)_2\text{O}$  and then dried in *vacuum* dessicator.

### Preparation of the Metal Complexes

A solution of the metal salts [1.0 mmol, 0.200 g for  $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$ , 0.250 g for  $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ , 0.250 g for  $\text{Ni}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ , 0.244 g for  $\text{VO}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$  and 0.220 g for  $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ ] in ethanol (10 cm<sup>3</sup>) was added to a solution of the ligands [2.0 mmol, 0.840 g for  $\text{H}_3\text{L}^1$ , 0.900 g for  $\text{H}_3\text{L}^2$  and 0.998 g for  $\text{H}_3\text{L}^3$ ] in ethanol (40 cm<sup>3</sup>) (in the VO(IV) complex, the pH of the solution fell to 1.9. It was adjusted with 0.1 M KOH in ethanol to ca 4.80 at which point precipitation of the complex occurred). The mixture was heated to 80°C while stirring. The mixture was left for 24 h at room temperature, the resulting solid was filtered, washed with cold ethanol, warm water and dried in a *vacuum* dessicator (see Table 1 for yields).

### Preparation of Microbial Culture

Sixteen compounds were evaluated for their in vitro antibacterial activity against *Enterobacter aerogenes* CCM 2531, *Enterococcus faecalis*



**Table 1.** Some analytical and physical data for the imine-oxime ligands and their complexes.

Compound	Color	Yield (%)	M.p. (°C)	Found (calc.)%				
				C	N	H	M	<sup>a</sup> Λ <sub>M</sub>
H <sub>3</sub> L <sup>1</sup>	light brown	84	182	62.90 (62.86)	13.37 (13.33)	4.78 (4.76)	—	1.8
Cu(L <sup>1</sup> ) <sub>2</sub>	brown	74	>300	58.61 (58.57)	12.45 (12.42)	4.25 (4.22)	7.10 (7.05)	7.4
Co(L <sup>1</sup> ) <sub>2</sub>	brown	70	>300	58.90 (58.87)	12.51 (12.49)	4.21 (4.24)	6.63 (6.57)	7.0
Ni(L <sup>1</sup> ) <sub>2</sub>	brown	67	226 <sup>b</sup>	58.91 (58.87)	12.53 (12.49)	4.26 (4.24)	6.61 (6.57)	8.7
VO(L <sup>1</sup> ) <sub>2</sub>	dark brown	60	204 <sup>b</sup>	58.39 (58.35)	12.44 (12.40)	4.23 (4.20)	5.69 (5.63)	6.8
Zn(L <sup>1</sup> ) <sub>2</sub>	yellow	70	184 <sup>b</sup>	58.42 (58.45)	12.45 (12.40)	4.17 (4.21)	7.30 (7.24)	9.0
H <sub>3</sub> L <sup>2</sup>	yellow	83	211	61.36 (61.33)	12.45 (12.44)	4.91 (4.89)	—	1.5
Cu(L <sup>2</sup> ) <sub>2</sub>	light brown	68	291 <sup>b</sup>	57.44 (57.41)	11.61 (11.65)	4.35 (4.37)	6.69 (6.61)	6.9
Co(L <sup>2</sup> ) <sub>2</sub>	brown	79	172 <sup>b</sup>	57.74 (57.70)	11.73 (11.70)	4.41 (4.39)	6.24 (6.16)	8.0
Ni(L <sup>2</sup> ) <sub>2</sub>	brown	72	211 <sup>b</sup>	57.67 (57.70)	11.74 (11.70)	4.43 (4.39)	6.23 (6.16)	7.2
VO(L <sup>2</sup> ) <sub>2</sub>	dark brown	65	196	57.25 (57.21)	11.58 (11.61)	4.31 (4.35)	5.34 (5.28)	8.5
Zn(L <sup>2</sup> ) <sub>2</sub>	yellow	65	201 <sup>b</sup>	57.34 (57.30)	11.60 (11.63)	4.40 (4.36)	6.85 (6.79)	10.0
H <sub>3</sub> L <sup>3</sup>	yellow	86	240	52.95 (52.91)	11.20 (11.22)	3.77 (3.81)	—	1.9
Cu(L <sup>3</sup> ) <sub>2</sub>	yellow	70	>300	49.86 (49.83)	10.60 (10.57)	3.45 (3.40)	6.07 (6.00)	7.3
Co(L <sup>3</sup> ) <sub>2</sub>	orange	68	>300	50.10 (50.05)	10.65 (10.62)	3.37 (3.41)	5.66 (5.59)	7.6
Ni(L <sup>3</sup> ) <sub>2</sub>	yellow	72	>300	50.03 (50.05)	10.60 (10.62)	3.44 (3.41)	5.67 (5.59)	8.5
VO(L <sup>3</sup> ) <sub>2</sub>	orange	71	283 <sup>b</sup>	49.72 (49.68)	10.58 (10.54)	3.35 (3.39)	4.87 (4.79)	7.9
Zn(L <sup>3</sup> ) <sub>2</sub>	yellow	68	>300	49.80 (49.75)	10.58 (10.55)	3.42 (3.39)	6.21 (6.16)	9.8

<sup>a</sup>Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>.

<sup>b</sup>Decompose.

ATCC 15753, *Pseudomonas aeruginosa* ATCC 27853, *Bacillus subtilis* ATCC 10 and *Mycobacterium smegmatis* CCM 2067 and antifungal activity against *Penicillium digitatum* by agar-well diffusion method. All bacteria were inoculated into Nutrient Broth (Difco) and incubated for 24 h, and the fungi studied inoculated in Malt Extract Broth (Difco) for 48h. In the agar-well diffusion method, Mueller Hinton Agar (Oxoid) for bacteria, and in Malt Extract Broth (Difco) sterilised in a flask and cooled to 45–50°C, was distributed (20 mL) to sterilised petri dishes after injecting 0.01 mL cultures of bacteria prepeared as mentioned above and allowed to solidify. The dilution plate method was used to enumerate microorganisms ( $10^5$  bacteria per mL) and fungi ( $10^3$ – $10^4$  per mL) for 24 h.<sup>[17]</sup> By using a sterilised cork borer (7 mm diameter), wells were dug in the culture plates. Compounds dissolved in DMF were added (0.2  $\mu$ L) to these wells. The petri dishes were left at 4°C for 2 h and then the plates were incubated at 30°C for bacteria (18–24 h) and at 25°C for fungi (72 h). At the end of the period, inhibition zones formed on the medium were evaluated is milimeters (mm). The control samples were only absorbed in DMF.

## RESULTS AND DISCUSSION

The starting metarial (A) for this research is prepared from commercially available starting materials, by the Schiff base condensation of 4-nitrobenzaldehyde and 4-aminothiophenol in a simple ratio. When the Schiff base ligand (A) is reduced, the amine compound (B) is obtained. It can easily decompose. Therefore, it was used as synthesized without further purification. The Schiff base ligands  $H_2B^1$ ,  $H_2B^2$  and  $H_2B^3$  are prepared from salicylaldehyde, *o*-vanillin and 5-bromosalicylaldehyde with the amine compound in a 1:1 molar ratio in a ethanolic solution, respectively, with subsequent removal of the excess amine with extraction into benzene. They are soluble in polar organic solvents such as EtOH, CHCl<sub>3</sub>, acetone, DMSO, DMF etc. Three novel *vic*-dioximes  $H_3L^1$ ,  $H_3L^2$  and  $H_3L^3$  were obtained by reaction of the imine compounds  $H_2B^1$ – $H_2B^3$  with monochloroglyoxime in the molar ratio 1:1. The resulting solids are intensely colored, and stable in air. The isolation of these compounds further highlights the utility of this methodology for the preparation of these types of compounds in a easy way with good yields. They are soluble in polar organic solvents such as EtOH, MeOH, DMSO, DMF etc., but generally only slightly soluble in CH<sub>2</sub>Cl<sub>2</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O and apolar hydrocarbon solvents. The oxime complexes containing the OH and OCH<sub>3</sub> groups are the most soluble compounds, whereas the Br substituted oxime complexes have

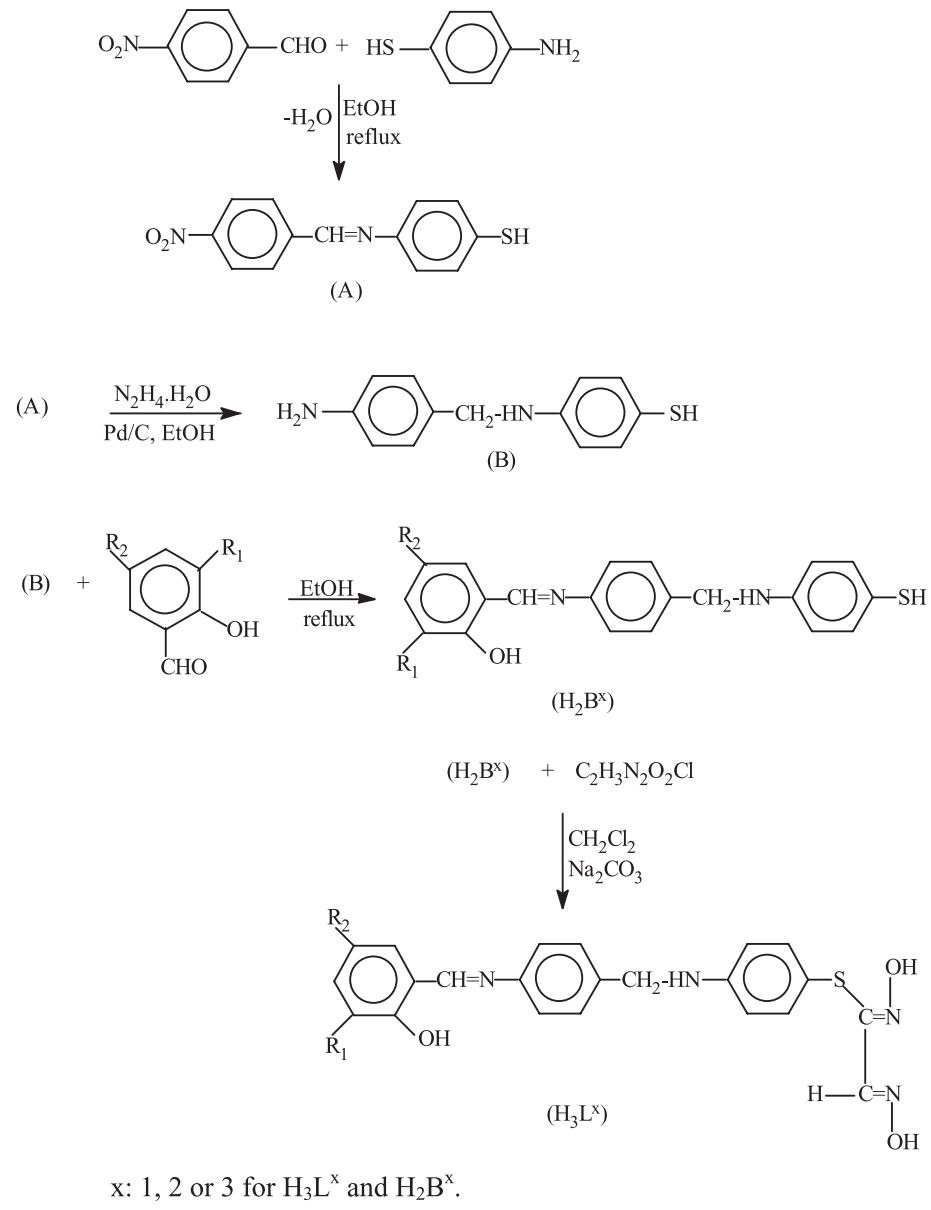


slightly soluble in organic solvents. All complexes are stable in air for months, some of the complexes have high melting points without decomposition up to 250°C. This situation may denote a strong bonding between the ligands and metal ion.  $H_3L^3$  is partially soluble in EtOH. Furthermore, the ligand solution was used as suspension during complexation. As the reaction proceeded in the presence of EtOH, the ligand dissolved completely, as shown by the color change of the reaction mixture. The molar conductivities in DMF ( $\sim 10^{-3}$  M solutions) are too small to account for any dissociation of the Schiff base ligands, *vic*-dioximes and complexes in the solvent. Therefore, they can be regarded as non-electrolytes. Looking at the elemental analysis results in Table 1, it is clear that the analytical data are in good agreement with the chemical formulae proposed for the compounds. Straightforward, clean and relatively high-yield synthetic routes to the pure ligands and complexes are outlined in Schemes 1 and 2.

IR spectroscopy is a powerful tool for structural determinations of ligands and metal chelates. In the ligands under investigation, functional groups OH, NH, CH=N, C-S, C=N-OH, O-H...O are of great importance in the infrared spectra.

Much has been written about the -OH stretching frequency and intensity of phenol derivatives that depend on many factors (e.g. substituents, medium...etc.). In the IR spectra of the ligands  $H_2B^1$ - $H_2B^3$  and  $H_3L^1$ - $H_3L^3$ , the band assigned to the stretching hydrogen motions in the intramolecular O-H...N hydrogen bonds appears broadened with a maximum in the range 2600–2610  $cm^{-1}$ . In the complexes, intramolecular hydrogen bonding (O-H...N) is present between the phenolic hydrogen and nitrogen of the azomethine group. This confirms that the phenolic C-OH and azomethine nitrogen are not coordinated to the metal ions.

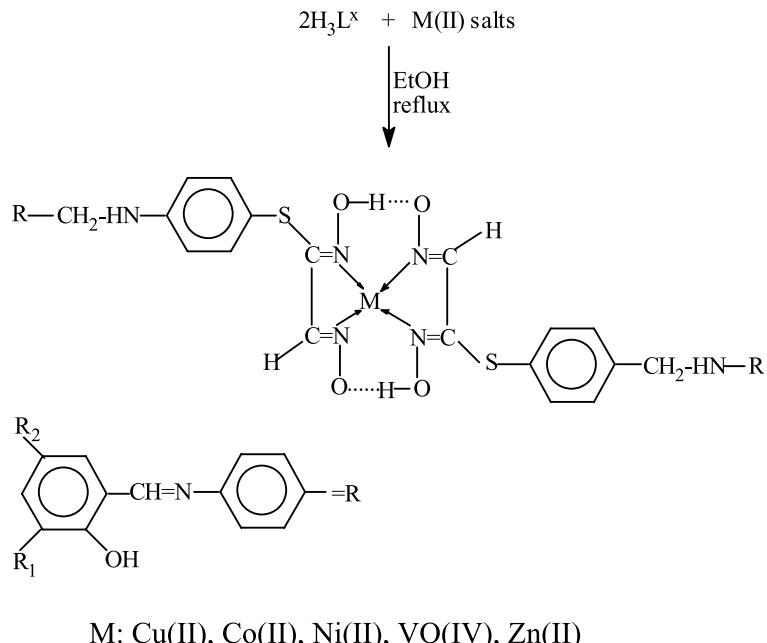
The infrared spectral bands most useful for determining Schiff base ligands  $H_2B^1$ - $H_2B^3$  and imine-oxime derivatives  $H_3L^1$ - $H_3L^3$  with metal complexes of these oximes are shown in Table 2. In the spectrum of the Schiff base ligand A, the strong band at 1516 and 1492  $cm^{-1}$  may be assigned to the characteristic  $\nu(NO_2)$  group and disappears during the formation of  $NH_2$  group. The spectrum of the amine compounds, exhibited two fairly strong bands at 3356 and 3213  $cm^{-1}$  attributable to the  $\nu(NH)$  and  $\nu(NH_2)$  vibrations of the primary and secondary amine groups, respectively.<sup>[18]</sup> The bands observed in the 1640–1632  $cm^{-1}$  range can be attributed to the azomethine group vibrations. In the oxime derivatives of these imine compounds, the vibration of the secondary amine, O-H and azomethine groups are approximately observed at the same region, but the S-H group is not observed. This situation confirms that the S-H group reacted with the monochloroglyoxime. In the oxime derivatives, the N-O and C=N stretching vibrations are at 956–943 and 1628–1622  $cm^{-1}$



	R <sub>1</sub>	R <sub>2</sub>
H <sub>3</sub> L <sup>1</sup>	H	H
H <sub>3</sub> L <sup>2</sup>	OMe	H
H <sub>3</sub> L <sup>3</sup>	H	Br

**Scheme 1.** Preparation of the ligands.





**Scheme 2.** Preparation of the metal complexes.

range, respectively. In the spectra of the complexes, the  $\text{C}=\text{N}$  stretching vibrations of the oximes are shifted to the  $1610\text{--}1595\text{ cm}^{-1}$  range. These observations indicate the involvement of the nitrogen atom of the azomethine ( $\text{C}=\text{N}$ ) group in the complexes.<sup>[19]</sup> In the complexes, the weak, broad bands in the range  $1745\text{--}1681\text{ cm}^{-1}$  can be ascribed to the intramolecular hydrogen bridge ( $\text{O}-\text{H}\cdots\text{O}$ ) bending vibrations. Disappearance of the stretching vibrations of ( $\text{O}-\text{H}$ ) band which was present in the free ligands is further evidence for ( $\text{O}-\text{H}\cdots\text{O}$ ) band formation.<sup>[20]</sup> All complexes show very strong and broad bands centered in the  $1610\text{--}1595\text{ cm}^{-1}$  range, corresponding to the  $\nu(\text{C}=\text{N})$  of the oxime group. These bands are probably broadened due to their overlap with the stretching of the aromatic ring-carbons. The IR data of these amorphous products show  $\nu(\text{V}-\text{O})$  at  $980\text{--}972\text{ cm}^{-1}$ , indicating monomeric structures. All complexes show very strong and broad bands centered in the  $1610\text{--}1595\text{ cm}^{-1}$  range, corresponding to the  $\nu(\text{C}=\text{N})$  of the oxime group. These bands are probably broadened due to their overlap with the stretching of the aromatic ring-carbons.

The electronic spectra of all compounds were recorded in EtOH. The wavelengths of the absorption maxima as well as the corresponding molar

**Table 2.** The infrared spectral data<sup>a</sup> for the ligands and their metal complexes (cm<sup>-1</sup>).

Compound	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu(\text{CH}_2)$	$\nu(\text{O}-\text{H}\dots\text{O})$	$\nu(\text{CH}=\text{N}-\text{OH})$	$\nu(\text{M}-\text{N})$
$\text{H}_3\text{L}^1$	3417 br	3216 w	2926 m	—	1624 s	—
$\text{Cu}(\text{L}^1)_2$	3423 br	3217 w	2924 m	1706 w	1606 s	501 w
$\text{Co}(\text{L}^1)_2$	3421 br	3228 w	2926 m	1703 w	1605 s	487 w
$\text{Ni}(\text{L}^1)_2$	3415 br	3230 w	2928 m	1726 w	1602 s	498 w
$\text{VO}(\text{L}^1)_2$	3422 br	3223 w	2926 m	1723 w	1600 s	480 w
$\text{Zn}(\text{L}^1)_2$	3424 br	3216 w	2930 m	1712 w	1600 s	497 w
$\text{H}_3\text{L}^2$	3344 br	3218 w	2930 m	—	1622 s	—
$\text{Cu}(\text{L}^2)_2$	3423 br	3221 w	2928 m	1702 w	1595 s	468 w
$\text{Co}(\text{L}^2)_2$	3425 br	3226 w	2931 m	1726 w	1600 s	503 w
$\text{Ni}(\text{L}^2)_2$	3421 br	3213 w	2935 m	1708 w	1610 s	516 w
$\text{VO}(\text{L}^2)_2$	3421 br	3225 w	2930 m	1713 w	1600 s	468 w
$\text{Zn}(\text{L}^2)_2$	3381 br	3240 w	2935 m	1730 w	1608 s	534 w
$\text{H}_3\text{L}^3$	3323 br	3219 w	2921 m	—	1628 s	—
$\text{Cu}(\text{L}^3)_2$	3425 br	3219 w	2954 m	1723 w	1610 s	513 w
$\text{Co}(\text{L}^3)_2$	3417 br	3223 w	2932 m	1720 w	1604 s	487 w
$\text{Ni}(\text{L}^3)_2$	3452 br	3228 w	2924 m	1727 w	1600 s	521 w
$\text{VO}(\text{L}^3)_2$	3430 br	3221 w	2926 m	1733 w	1602 s	493 w
$\text{Zn}(\text{L}^3)_2$	3432 br	3218 w	2926 m	1719 w	1600 s	502 w

<sup>a</sup>br (broad), s (strong), m (medium), w (weak).

extinction coefficients ( $\epsilon$ ) are given in Table 3. A clear analogy is evident among the results for all compounds. In the spectra of the ligands  $\text{H}_2\text{B}^1-\text{H}_2\text{B}^3$ , the  $\pi-\pi^*$  transitions in the range 297–210 nm are not significantly altered on complex formation and are omitted from Table 3. The  $n-\pi^*$  transitions associated with azomethine of oximes are found in the range 368–311 nm. In the spectra of the complexes, the  $n-\pi^*$  transitions are shifted to higher energy. These results indicate that the nitrogen atoms of the oxime groups are coordinated to the metal ions.<sup>[21]</sup> In the spectra of the Cu(II) complexes, the d–d transitions are observed in the 576–545 nm range. These values are of particular importance since they were highly dependent on the geometry of the molecule. It is known that the transition from a square-planar structure to a deformed tetrahedral structure leads to a red shift of absorption in the electronic spectra.<sup>[22]</sup> Thus, the smaller value of the wavelength of the band corresponding to the transitions, is due to the resemblance between the geometry of the complex and that of the square-planar complex. Consequently, the larger values of the ligands  $\text{H}_3\text{L}^1-\text{H}_3\text{L}^2$ , indicate that the geometry resembles that of a deformed tetrahedral structure. Usually, the electronic spectra of the square-pyramidal VO(IV) complexes ( $d^1$ ) are characterized by the presence of three absorption bands



**Table 3.** The electronic absorption spectral data and magnetic moments of the imine–oxime ligands and their metal complexes.

Compound	$\mu_{\text{eff}}$ (B.M.)	$\lambda_{\text{max}}$ ( $\epsilon$ , $M^{-1}cm^{-1}$ )
$H_3L^1$		357 ( $3.0 \times 10^3$ ), 320 ( $1.7 \times 10^3$ ), 293 ( $6.6 \times 10^4$ ), 216 ( $9.1 \times 10^4$ )
$Cu(L^1)_2$	1.84	545 (230), 331 ( $2.2 \times 10^3$ ), 312 ( $5.8 \times 10^3$ ), 301 ( $1.1 \times 10^3$ ), 210 ( $4.0 \times 10^4$ )
$Co(L^1)_2$	4.40	645 (128), 529 (637), 359 ( $2.9 \times 10^3$ ), 316 ( $5.7 \times 10^3$ ), 297 ( $7.3 \times 10^3$ ), 211 ( $8.5 \times 10^4$ )
$Ni(L^1)_2$	Diamag.	627 (364), 357 ( $3.3 \times 10^3$ ), 351 ( $7.0 \times 10^3$ ), 345 ( $1.5 \times 10^3$ ), 317 ( $4.9 \times 10^3$ ), 291 ( $1.8 \times 10^4$ )
$VO(L^1)_2$	1.80	787 (120), 348 ( $6.5 \times 10^3$ ), 319 ( $2.7 \times 10^4$ ), 293 ( $5.2 \times 10^4$ )
$Zn(L^1)_2$	Diamag.	359 ( $3.7 \times 10^3$ ), 319 ( $1.1 \times 10^3$ ), 294 ( $3.2 \times 10^4$ ), 211 ( $7.7 \times 10^4$ )
$H_3L^2$		363 ( $5.2 \times 10^3$ ), 351 ( $6.3 \times 10^3$ ), 311 ( $8.3 \times 10^3$ ), 225 ( $5.0 \times 10^4$ )
$Cu(L^2)_2$	1.80	549 (361), 371 ( $4.7 \times 10^3$ ), 261 ( $1.2 \times 10^4$ ), 223 ( $1.8 \times 10^4$ )
$Co(L^2)_2$	4.37	666 (223), 584 (347), 369 ( $7.2 \times 10^3$ ), 313 ( $5.4 \times 10^3$ ), 225 ( $3.4 \times 10^4$ )
$Ni(L^2)_2$	Diamag.	635 (254), 383 ( $3.5 \times 10^3$ ), 352 ( $7.2 \times 10^4$ ), 315 ( $6.9 \times 10^4$ )
$VO(L^2)_2$	1.77	781 (263), 316 ( $7.7 \times 10^3$ ), 261 ( $6.5 \times 10^3$ ), 220 ( $1.2 \times 10^4$ )
$Zn(L^2)_2$	Diamag.	374 ( $8.0 \times 10^3$ ), 351 ( $9.4 \times 10^3$ ), 316 ( $5.7 \times 10^4$ )
$H_3L^3$		368 ( $3.7 \times 10^3$ ), 320 ( $4.8 \times 10^3$ ), 293 ( $1.8 \times 10^3$ ), 266 ( $3.8 \times 10^3$ ), 219 ( $7.2 \times 10^4$ )
$Cu(L^3)_2$	1.88	576 (213), 348 ( $3.8 \times 10^3$ ), 314 ( $5.7 \times 10^3$ ), 296 ( $1.9 \times 10^3$ )
$Co(L^3)_2$	4.41	658 (327), 532 (536), 381 ( $1.1 \times 10^3$ ), 292 ( $7.0 \times 10^3$ ), 276 ( $5.8 \times 10^4$ )
$Ni(L^3)_2$	Diamag.	628 (300), 377 ( $5.5 \times 10^3$ ), 313 ( $1.8 \times 10^3$ ), 266 ( $2.2 \times 10^4$ )
$VO(L^3)_2$	1.75	768 (120), 369 ( $1.5 \times 10^3$ ), 323 ( $1.3 \times 10^3$ ), 294 ( $3.5 \times 10^4$ )
$Zn(L^3)_2$	Diamag.	369 ( $5.7 \times 10^3$ ), 320 ( $1.5 \times 10^4$ ), 294 ( $1.0 \times 10^4$ )

corresponding to  $d_{xy} \rightarrow d_{xz}$ ,  $d_{yz}$ ,  $d_{xy} \rightarrow d_{x2-y2}$ ,  $d_{xy} \rightarrow d_{z2}$  transitions.<sup>[23]</sup> Similarly, in the electronic spectra of the present complexes, the absorption bands were observed in the range 787–768 nm and may be assigned to the d–d transitions.

The magnetic moments (as B.M.) of the complexes were measured at room temperature, magnetic moment data for the complexes are given in Table 3. The structures of the monomeric complexes are supported by magnetic moment data. The Ni(II) and Zn(II) complexes of the ligands  $H_3L^1$ – $H_3L^3$  have diamagnetic character and square-planar and tetrahedral geometry around the metal ions. The magnetic moments of the Cu(II) complexes have values in the 1.80–1.88 B.M. range and lie in the interval expected for the Cu(II) chelates. These values suggest that the copper atom is in a tetrahedral environment in its chelates.<sup>[24,25]</sup>

The magnetically dilute VO(IV) complexes usually exhibit magnetic moments close to their spin-only value of 1.73 B.M.. Magnetic moments of the VO(IV) complexes are in the range of 1.75–1.80 B.M.. Due to steric interactions of the larger size of the ligands, the lower coordination number five has been assigned to these complexes. The *vic*-dioxime complexes of the VO(IV) may have the usual tetragonal pyramidal structure.

The Co(II) complexes of the imine–oxime ligands  $H_3L^1$ ,  $H_3L^2$  and  $H_3L^3$  have the values 4.40, 4.37 and 4.41 B.M., respectively, and these values indicate that the Co(II) ion has tetrahedral nature around the metal ion.

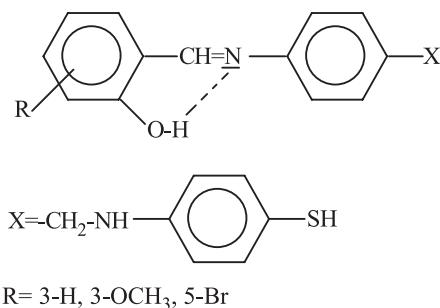
Additional structural information can be deduced from the  $^1H$ – and  $^{13}C$ -NMR spectra (Table 4). In Schiff base ligands  $H_2B^1$ – $H_2B^3$ , there is a proton donor OH group and one proton acceptor group in the ortho position. Due to presence of the OH groups in the ortho position to the imine group, formation of a few intramolecular hydrogen bond is possible. Hydrogen bond formation is shown in Figure 1. The OH resonance and azomethine protons are present in the *vic*-dioxime ligands and their metal complexes without further change. This conclusion is supported by other spectroscopic methods. For  $^1H$ – and  $^{13}C$ -NMR data, labelling of the atoms of the ligands  $H_3L^1$ – $H_3L^3$  is given in Figure 2. It is important to emphasize the  $^1H$  resonance of the O–H group in the 11.40–10.35 ppm range. The signal due to the OH proton disappears in  $D_2O$  solution. In the imine ligands, the sharp signals in the 8.40–8.63 ppm range can be attributed to the azomethine proton. For the imine–oxime ligands  $H_2B^1$ – $H_2B^3$ , these OH and azomethine signals are observed at in approximately the same regions. In the Ni(II) and Zn(II) imine–oxime complexes, the peak(s) due to  $CH=N$  group do not show any shift, and this situation confirms that these groups are not coordinated to metals. In addition, the proton of the phenolic oxygen atoms remain and this situation confirms that these OH groups are not coordinated to the metal ions are apparently not coordinated



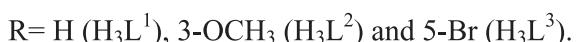
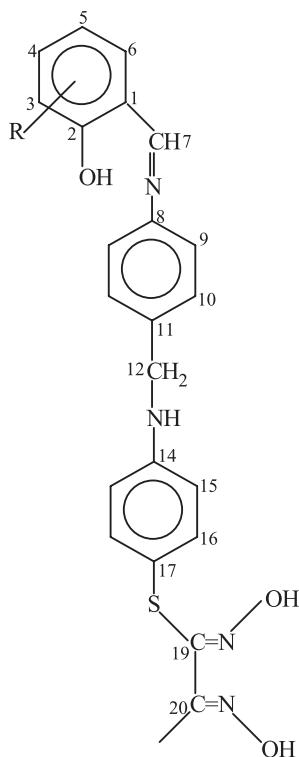
**Table 4.** The  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. data (as p.p.m.) for the Schiff base and imine–oxime ligands using  $\text{DMSO-d}_6$  as solvent.

No	$^{13}\text{C-NMR}$ ( $\text{H}_3\text{L}^1$ )	$^{13}\text{C-NMR}$ ( $\text{H}_3\text{L}^2$ )	$^{13}\text{C-NMR}$ ( $\text{H}_3\text{L}^3$ )	$^1\text{H-NMR}$ ( $\text{H}_3\text{L}^1$ )	$^1\text{H-NMR}$ ( $\text{H}_3\text{L}^2$ )	$^1\text{H-NMR}$ ( $\text{H}_3\text{L}^3$ )
1	119.5	117.61	119.71	–	–	–
2	161.41	151.70	158.33	–	–	–
3	117.2	149.50	118.46	7.01	–	6.88
4	133.90	122.60	137.04	7.25	7.17	7.32
5	119.55	115.50	157.64	7.20	7.18	–
6	133.25	121.90	130.80	7.20	7.20	6.54
7	164.25	161.89	163.26	8.42	8.44	8.38
8	153.46	153.32	152.99	–	–	–
9	121.21	121.22	121.21	7.05	7.02	7.01
10	129.82	129.89	129.82	7.25	7.24	7.23
11	138.18	138.15	138.17	–	–	–
14	48.42	48.43	48.40	3.41	3.43	3.40
15	154.19	154.18	154.19	–	–	–
16	118.25	118.20	118.22	6.80	6.82	6.75
17	131.07	131.07	131.09	7.46	7.44	7.40
18	131.50	131.49	131.51	–	–	–
21	162.41	162.40	162.41	–	–	–

to metals. In the imine ligands, the singlets in the 3.34–3.56 ppm range are assigned to the proton of the SH group, whereas in the imine–oxime ligands, this signal disappears, further confirming the reaction of the SH group and monochloroglyoxime. The protons of the benzene rings are observed in the 6.20–7.70 ppm range as multiplets. In the spectra of the imine and oxime ligands, these multiplets are observed at approximately



**Figure 1.** Formation of hydrogen bond among nitrogen atom and OH group.



**Figure 2.** Labelling of the atoms of the *vic*-dioxime ligands.

same region. The triplets in 5.34–5.57 ppm range may be assigned to the NH protons. The NH proton can be identified very easily, because of the disappearances of the chemical shifts of protons on D<sub>2</sub>O exchange. In the low-frequency region, three broad signal lines assigned to the CH<sub>2</sub> protons and one sharp resonance signal of the OCH<sub>3</sub> group protons are observed. In the spectra of the ligands H<sub>3</sub>L<sup>1</sup>–H<sub>3</sub>L<sup>3</sup>, the deuterium exchangeable protons of the =N–OH groups show a chemical shifts in 14.30, 14.85 and 15.50 ppm, respectively, as a singlet which indicates an (E,E)–structure for the vicinal dioxime.<sup>[26]</sup> In the spectra of the Ni(II) and Zn(II) complexes, the deuterium is exchangeable, and intramolecular bridging O–H...O protons appear as a singlets at 15.20–16.20 ppm range. This situation indicates that the nitrogen atoms of the oxime group are coordinated to the metal ions.



Proton-decoupled  $^{13}\text{C}$ -nmr spectroscopy is very useful for distinguishing metal complexes. In the spectra of the Schiff base ligands  $\text{H}_2\text{B}^1\text{--H}_2\text{B}^3$ , the signals in the 160.50–162.10, 112.10–157.40 and 60.40–61.40 ppm range may be assigned to the azomethine, aromatic rings and  $\text{CH}_2$  groups, respectively. In the oxime ligands, these signals do not shift downfield or upfield. The carbon atoms of the oxime group are observed in the 164.90–165.47 ppm range. The proton-decoupled  $^{13}\text{C}$ -nmr spectra of the Ni(II) and Zn(II) complexes occur as a singlets in the 166.48–168.35 ppm range, corresponding to the two equivalent *vic*-dioxime ligands and therefore suggest that the two *vic*-dioxime are trans to each other. In fact, only one signal is observed for coordination to chelating nitrogen donors which has been the subject of considerable interest in literature.<sup>[27]</sup> In addition, in the complexes, the carbon atoms of the benzenoid rings are observed at 112.10–158.80 ppm range.

We have already made numerous efforts to crystallize any complex of the oxime ligands for X-ray diffraction studies. However, up till now, no single crystals have been obtained. In this way, it would be possible to determine the coordination of the ligands.

The relatively small intensities of the molecular ion peaks,  $[\text{M}]^+$ , are indicative of the case of fragmentation of the compounds, and this may reflect the number of heteroatoms present in each structure. The imine–oxime ligands show similar FAB mass spectra. In the free ligands, the molecular ion peaks,  $[\text{H}_3\text{L}^n + 1]^+$  ( $n$ : 1, 2 or 3), were observed at  $m/z$  421, 451 and 500. The observation of peaks related to fragments of the type  $\text{H}_3\text{L}^n$  ( $n$ : 1, 2 or 3) at  $m/z$  333, 363 and 412 for imine–oxime ligands indicate that the *vic*-dioxime fragment loss from the ligands. For the ligands  $\text{H}_3\text{L}^1$ ,  $\text{H}_3\text{L}^2$  and  $\text{H}_3\text{L}^3$ , the highest intensity peaks at  $m/z$  208, 238 and can be attributed to the ions of the  $[\text{2-OH-Ph-CH=N-Ph-CH}_2]^{+2}$ ,  $[\text{3-OCH}_3\text{-2-OH-Ph-CH=N-Ph-CH}_2]^{+2}$ ,  $[\text{5-Br-2-OH-Ph-CH=N-Ph-CH}_2]^{+2}$ , respectively. In other words, the relatively low intensity peaks at  $m/z$  123, 107, 105 and 87 may be assigned to the  $[\text{HN-Ph-S}]^{+2}$ ,  $[\text{2-OH-Ph-CH}_2]^{+2}$ ,  $[\text{NH-Ph-CH}_2]^{+2}$  and  $[\text{C}_2\text{H}_3\text{N}_2\text{O}_2]^{+2}$  ions.

The coordination of the imine–oxime ligands to the metals are also confirmed by the FAB mass spectra. All compounds show parent peaks related to the  $[\text{M(L}^n\text{)}_2]^+$  fragments. The base peaks in the  $m/z$  895–1054 and 902–1061 ranges correspond to the singly protonated species  $[\text{H} + \text{M(L}^n\text{)}_2]^+$  which are formed by reaction with the acetic acid in the mobile phase. In the spectra of the Ni(II) and Zn(II) complexes, the strong peaks at  $m/z$  230 and 237 can be attributed to the  $[(\text{C}_2\text{H}_2\text{N}_2\text{O}_2)_2\text{M}]^{+2}$ , M: Ni(II) and Zn(II), ions, respectively.

Synthetized compounds were tested for in vitro antimicrobial activity by the agar-well diffusion method. The antibacterial and antifungal

Table 5. Antimicrobial effects of the ligands and their metal complexes.<sup>a</sup>

Compound	Microorganisms (Inhibition zone <sup>b</sup> )						
	<i>E. faecalis</i>	<i>E. aerogenes</i>	<i>P. aeruginosa</i>	<i>B. subtilis</i>	<i>M. smegmatis</i>	<i>P. digitatum</i>	Control
$\text{Cu}(\text{L}^1)_2$	—	11	—	—	—	—	—
$\text{Co}(\text{L}^1)_2$	—	12	—	—	—	—	—
$\text{Ni}(\text{L}^1)_2$	—	10	—	—	—	—	—
$\text{VO}(\text{L}^1)_2$	—	10	—	—	—	—	—
$\text{Zn}(\text{L}^1)_2$	—	—	—	—	12	—	—
$\text{Cu}(\text{L}^2)_2$	—	14	—	—	—	—	—
$\text{Co}(\text{L}^2)_2$	—	—	—	11	—	—	—
$\text{Ni}(\text{L}^2)_2$	—	—	—	—	—	—	—
$\text{VO}(\text{L}^2)_2$	—	—	—	12	—	—	—
$\text{Zn}(\text{L}^2)_2$	—	—	—	11	—	—	—
$\text{H}_3\text{L}^3$	—	16	9	17	12	—	—
$\text{Cu}(\text{L}^3)_2$	—	16	—	—	—	—	—
$\text{Co}(\text{L}^3)_2$	—	15	—	—	—	—	—
$\text{Ni}(\text{L}^3)_2$	—	15	—	—	—	—	—
$\text{VO}(\text{L}^3)_2$	—	14	—	—	13	—	—
$\text{Zn}(\text{L}^3)_2$	—	14	—	14	—	—	—

The symbol ‘—’ indicates no zone of inhibition.

<sup>a</sup>Conc. = 100 µg/well.

<sup>b</sup>Including well diameter (7 mm).

activities of the compounds against five bacteria and the fungi are presented in Table 5. Also included is the activity of the solvent DMF. It was observed that all the compounds tested showed no antifungal activity. Also, the compounds were not effective against the growth of *Enterococcus faecalis*. Of the compounds tested 8 to 11 and 16 inhibited the growth of *Enterobacter aerogenes*, showing an inhibition zone of 10–16 mm (Table 5). Only one compound inhibited the growth of *Pseudomonas aeruginosa*, with an inhibition zone of 9 mm. Three compounds have antimicrobial activity against *Mycobacterium smegmatis* and five compounds against *Bacillus subtilis* as shown in Table 5.

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