

# Synthesis and Spectrophotometric Investigation of a New *vic*-Dioxime Ligand and Its Transition Metal Complexes\*

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A new *vic*-dioxime ligand and its Cu(II), Co(II), Ni(II), Pd(II), VO(IV) and Zn(II) complexes have been prepared and characterized by elemental analyses, infrared, electronic spectra, magnetic moment and molar conductance data. The Ni(II), Pd(II) and Zn(II) complexes have a diamagnetic character. The <sup>1</sup>H- and <sup>13</sup>C-nmr and GC/MS spectra of the *vic*-dioxime ligand and its Ni(II), Pd(II) and Zn(II) complexes were recorded. In addition, all compounds are non-electrolyte.

## Introduction

*vic*-Dioximes have received considerable attention as model compounds which mimic biofunctions such as the reduction of vitamin B<sub>12</sub><sup>1,2</sup>. Oxime metal chelates are biologically active<sup>3</sup> and semiconducting<sup>4,5</sup>. The chemistry of *vic*-dioxime transition metal complexes have been studied and is the subject of several reviews<sup>2,6</sup>.

Amines or mercaptans react with (E,E)-dichloroglyoxime or cyanogen-di-*N*-oxide to yield various heterocyclic and macrocyclic *vic*-dioximes<sup>7-11</sup>. The (E,E)- and (E,Z)-stereoisomers of *vic*-dioximes coordinate through their N,N or N,O sites and in a few cases, interconversion of (E,E)- and (E,Z)-complexes<sup>12-15</sup> is possible. Tschugaef<sup>16</sup> was the first to identify the bidentate nature of *vic*-dioximes in his significant work on the reaction between nickel(II) salts and dimethylglyoximes. Transition metal complexes of these *vic*-dioximes are essentially N,N-coordinated square-planar structures, but the uranyl complexes form  $\mu$ -hydroxo-bridged dimers with N,O-coordination as shown by infrared and <sup>1</sup>H-nmr spectroscopy<sup>17,18</sup>.

This article describes the synthesis and characterization of a new *vic*-dioxime and its transition metal complexes.

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## Experimental

### Materials

All organic solvents and metal salts used for synthesis and physical measurements were reagent grade and were used without further purification. 4-nitrobenzaldehyde, KOH, 4-nitroaniline, Pd/C (10%) and hydrazinium hydrate (100%) were used as supplied from Fluka. Monochloroglyoxime was prepared as described in the literature<sup>19</sup>.

### Physical Measurements

Elemental analyses (C, H, N) were performed using a Leco 932 elemental analyzer. Infrared spectra were obtained using KBr discs (4000-400  $\text{cm}^{-1}$ ) 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  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as calibrant. Molar conductances of the *vic*-dioxime ligand and its transition metal complexes were determined in DMSO ( $\sim 10^{-3}$  M) at room temperature using a Jenway Model 4070 conductivity meter. The mass spectra analyses were carried out on a Nicromass 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 was directly injected into an API-II (equipment for atomic 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  $\text{cm}^3 \text{min}^{-1}$ . Pressure in the mass analyzer region was usually about  $5 \times 10^{-3}$  Pa.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were taken on a Varian XL-200 NMR instrument. TMS was used as internal standard and deuterated dimethyl sulphoxide as solvent. The metal contents of the complexes were determined by an Ati Unicam 929 Model AA Spectrometer in solutions prepared by decomposing the compounds in aqua regia and subsequently digesting them in concentrated HCl.

### Preparation of Schiff Base Ligand

The Schiff base ligand HL was prepared by condensation of the 4-nitroaniline (1 mmol, 0.138 g) with the 4-nitrobenzaldehyde (1 mmol, 0.151 g) in EtOH (40  $\text{cm}^3$ ) achieved by boiling the mixture under reflux for 1 h. The precipitated ligand was filtered off, recrystallized from acetone/hexane (v/v) and dried in a vacuum dessicator.

**HL:** Yield: 0.25 g (90%), light yellow crystals, m.p. 198°C. Electronic spectrum (EtOH,  $\lambda_{max}/\text{nm}$ ): 339, 301, 210. FT-IR (KBr,  $\text{cm}^{-1}$ ): 1620 (C=N), 1558, 1498 ( $\text{NO}_2$ ).  $^1\text{H}$ -NMR (DMSO- $d_6$ , TMS,  $\delta$  ppm): 8.30 (1H, s, CH=N), 6.20-7.15 (8H, m, Ar-H).  $^{13}\text{C}$ -NMR (DMSO- $d_6$ , TMS,  $\delta$  ppm): 167.05 (CH=N), 110.00-152.47 (Ar-C). Analysis: found: C, 48.42; H, 2.77; N, 13.09%. Calculated for  $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_4$  (322): C, 48.45; H, 2.80; N, 13.04%.

### Preparation of the Amine Compound

The ligand HL (2 mmol, 0.542 g) was dissolved in EtOH (100  $\text{cm}^3$ ) and the solution was heated to 80°C. A quantity of 0.70 g of Pd/C (10%) was then added to this solution at the same temperature and 20  $\text{cm}^3$  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 yellow product was extracted with chloroform. The extract was reduced under vacuum and cooled in a refrigerator at  $-10^{\circ}\text{C}$ . The formed crystals were filtered and washed with cold hexane.

**HL<sup>1</sup>**: Yield: 0.46 g (80%), light red crystals, m.p.  $162^{\circ}\text{C}$ . Electronic spectrum (EtOH,  $\lambda_{max}/\text{nm}$ ): 451, 375, 352, 285, 236. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3419 (NH<sub>2</sub>), 3246 (NH), 2937 (CH<sub>2</sub>).

### Preparation of Vic-Dioxime Ligand (HL<sup>2</sup>)

The new *vic*-dioxime ligand (HL<sup>2</sup>) was prepared according to the procedure described 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 Na<sub>2</sub>CO<sub>3</sub> (25 cm<sup>3</sup>), was added with stirring to a solution of the ligands HL<sup>1</sup> (5 mmol, 1.065 g) in CH<sub>2</sub>Cl<sub>2</sub> (80 cm<sup>3</sup>) at room temperature. The reaction was continued for 10 h at the above temperature and the resulting compound was separated by filtration and washed with cold CH<sub>2</sub>Cl<sub>2</sub> and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O and then dried in a vacuum dessicator.

**HL<sup>2</sup>**: Yield: 0.18 g (47%), dark yellow crystals, m.p.  $140^{\circ}\text{C}$ . Electronic spectrum (EtOH,  $\lambda_{max}/\text{nm}$ ): 457, 347, 314, 215. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3232 (NH), 2978 (CH<sub>2</sub>), 1604 (C=N-OH), 974 (N-O). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 16.30, 16.32 (4H, s, O-H proton of the oxime group), 6.25-7.37 (8H, m, Ar-H), 5.17 (2H, s, NH), 5.10 (1H, t, NH), 2.67 (2H, d, CH<sub>2</sub>). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 167.85 (C=N-OH), 112.35-155.74 (Ar-C), 61.15 (CH<sub>2</sub>). Analysis: found: C, 53.03; H, 5.00; N, 25.47%. Calculated for C<sub>17</sub>H<sub>19</sub>N<sub>7</sub>O<sub>4</sub> (385): C, 52.99; H, 4.94; N, 25.45%. MS(EI):m/z= 386 ([M+H]<sup>+</sup>, 40%), 87 ([M-CH<sub>2</sub>H<sub>3</sub>N<sub>2</sub>O<sub>2</sub>]<sup>+</sup>, 57%).

**NiL<sup>2</sup>**: <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 16.4 (2H, s, O-H...O proton of the oxime group), 6.18-7.43 (8H, m, Ar-H), 5.7 (2H, s, NH), 5.1 (1H, t, NH protons bound to the CH<sub>2</sub> group), 2.65 (2H, d, CH<sub>2</sub>). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 168.67 (C=N-OH), 112.7-156.2 (Ar-C), 61.2 (CH<sub>2</sub>). MS(FAB): m/z= 884 (M<sup>+</sup>, 24%).

**PdL<sup>2</sup>**: <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 15.9 (2H, s, O-H...O proton of the oxime group), 6.2-7.45 (8H, m, Ar-H), 5.9 (2H, s, NH), 5.1 (1H, t, NH protons bound to CH<sub>2</sub> group), 2.68 (2H, d, CH<sub>2</sub>). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 168.5 (C=N-OH), 112.8-158.7 (Ar-C), 61.1 (CH<sub>2</sub>). MS(FAB): m/z= 980 (M<sup>+</sup>, 30%).

**ZnL<sup>2</sup>**: <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 15.7 (2H, s, O-H...O proton of the oxime group), 6.23-7.50 (8H, m, Ar-H), 5.8 (2H, s, NH), 5.2 (1H, t, NH protons bound to CH<sub>2</sub> group), 2.63 (2H, d, CH<sub>2</sub>). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 168.14 (C=N-OH), 112.8-156.4 (Ar-C), 61.1 (CH<sub>2</sub>). MS(FAB): m/z= 898 (M<sup>+</sup>, 20%).

### Preparation of the Cu(II), Co(II), Ni(II), VO(IV) and Zn(II) Complexes

A solution of the metal salts [1.0 mmol, 0.200 g for Cu(AcO)<sub>2</sub>·H<sub>2</sub>O, 0.238 g for CoCl<sub>2</sub>·6H<sub>2</sub>O, 0.250 g for Ni(AcO)<sub>2</sub>·4H<sub>2</sub>O, 0.244 g for VO(SO<sub>4</sub>)·5H<sub>2</sub>O and 0.173 g for ZnCl<sub>2</sub>·2H<sub>2</sub>O] in ethanol (10 cm<sup>3</sup>) was added to a solution of the ligand HL<sup>2</sup> [1.0 mmol, 0.385 g] 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  $80^{\circ}\text{C}$  while stirring. The mixture was left for 24 h at

room temperature, and the resulting solid was filtered off, washed with cold ethanol and warm water and dried in a vacuum dessicator (see Table 1 for yields).

**Table 1.** Some Analytical and Physical Data for the *vic*-Dioxime Complexes.

Compound	Colour	Yield	M.p.		Calcd.(found) %				
			C	H	N	M	<sup>a</sup> Λ <sub>M</sub>		
CuL <sup>2</sup>	Brown	58	>250	45.68 (45.71)	3.81 (3.76)	21.95 (21.98)	14.23 (14.30)	9.4	
CoL <sup>2</sup>	Brown	61	>250	46.16 (46.14)	3.85 (3.90)	22.17 (22.14)	13.33 (13.39)	9.1	
NiL <sup>2</sup>	Brown	65	>250	46.15 (46.10)	3.84 (3.82)	22.16 (22.15)	13.34 (13.42)	8.7	
PdL <sup>2</sup>	Orange	60	>250	41.68 (41.71)	3.47 (3.51)	20.02 (20.05)	21.74 (21.83)	9.0	
VOL <sup>2</sup>	Brown	62	>250	45.34 (45.37)	3.78 (3.81)	21.78 (21.74)	21.78 (21.93)	10.0	
ZnL <sup>2</sup>	Orange	62	>250	45.50 (45.56)	3.79 (3.75)	21.86 (21.83)	14.58 (14.64)	8.8	

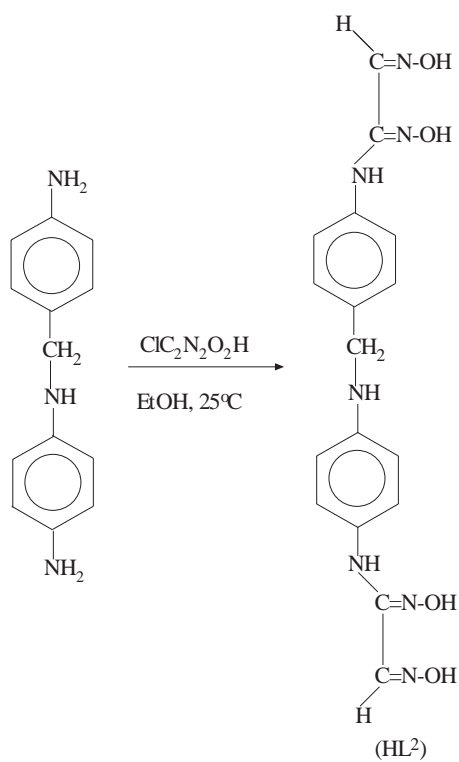
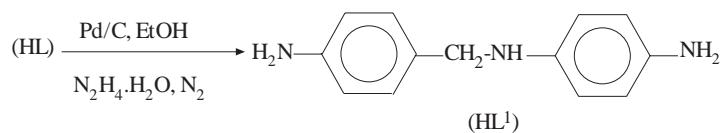
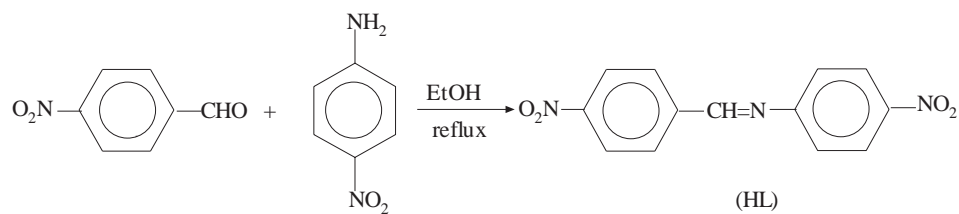
a: Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>.

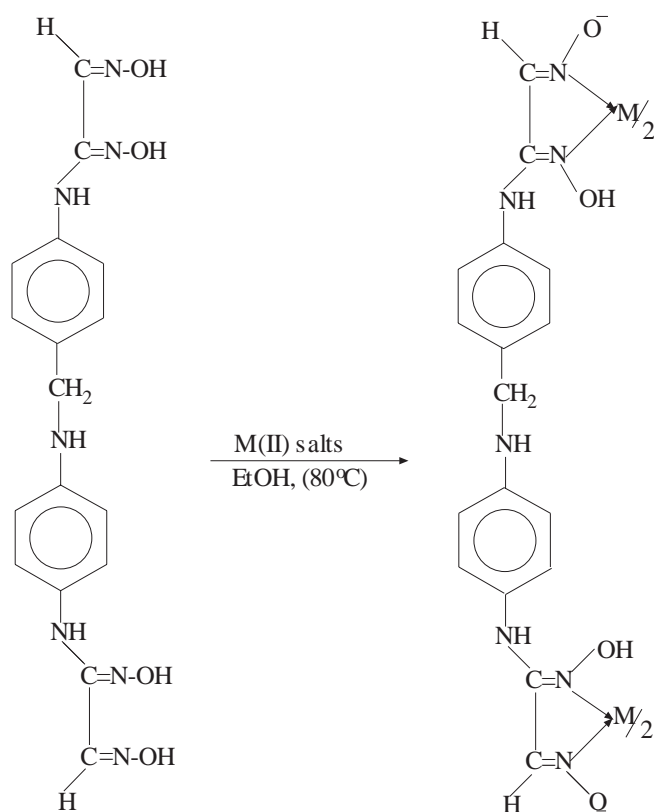
## Pd(II) Complexes

To a weighed amount of the Pd(II) acetate (1 mmol, 0.225 g), the calculated amount of the ligand HL<sup>2</sup> [1 mmol, 0.385 g] was added in a 1:1 (M:L) molar ratio using acetic acid (15 cm<sup>3</sup>) as solvent. The solution was stirred for 3 h. The precipitated complex was filtered, washed with warm water and then several times with cold EtOH and dried in vacuo over P<sub>4</sub>O<sub>10</sub> (see Table 1 for yield).

## Results and Discussion

The starting material (HL) for this research is prepared by reacting the 4-nitrobenzaldehyde and 4-nitroanilin. The amine compound obtained by reducing the ligand HL is not stable at room temperature. Therefore, the amine compound was used as obtained without further purification. In addition, it is soluble in polar organic solvents such as EtOH, CHCl<sub>3</sub>, acetone, DMSO and DMF. Novel *vic*-dioxime was obtained by reaction of the amine compound with monochloroglyoxime in the molar ratio 1:2. The resulting solid is intensively coloured, and stable in air. It is more soluble in polar organic solvents such as EtOH, MeOH, DMSO and DMF. 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 hydrocarbon solvents. The oxime complexes are slightly soluble in polar organic solvents such as EtOH, MeOH, DMSO, DMF, THF and dioxan. Although the ligand HL<sup>2</sup> has polar groups such as OH and -C=N, the solubility of the complexes is poor in polar and apolar organic solvents. Therefore, it is possible to suggest that the complexes have a polymeric nature<sup>20</sup>. All complexes are stable in air for months. The molar conductivities in DMF (~10<sup>-3</sup> M solutions) are too small to account for any dissociation of the *vic*-dioxime ligand and oxime complexes in the solvent. Therefore, they can be regarded as non-electrolytes<sup>21</sup>. The analytical data (see Table 1) are in good agreement with the chemical formulae proposed for the compounds. The routes for the synthesis of the Schiff base ligand, amine compound, *vic*-dioxime and metal complexes are given in the Scheme.





M= Cu(II), Co(II), Ni (II), Pd(II), VO(IV) and Zn(II)

**Scheme.** Preparation of the ligands and complexes.

The infrared spectral bands most useful for determining metal complexes of these oximes are shown in Table 2. In the spectra of the Schiff base ligand, the strong bands in the  $1558\text{--}1498\text{ cm}^{-1}$  region may be assigned to the characteristic  $\nu(\text{NO}_2)$  group, and disappear during the formation of  $\text{NH}_2$  group. In the spectra of the amine compounds, all exhibited two fairly strong bands between  $3419$  and  $3246\text{ cm}^{-1}$  attributable to the  $\nu(\text{NH})$  and  $\nu(\text{NH}_2)$  vibrations of the primary and secondary amine groups, respectively<sup>22</sup>. In the oxime derivative of this amine compound, the vibrations of the secondary amine groups are approximately observed in the same region, but the primary amine groups are shifted to the lower regions. This situation confirms that the primary amine groups reacted with the monochloroglyoxime. The (O-H) stretching vibration is observed in the  $3600\text{--}3406\text{ cm}^{-1}$  range as broad absorptions. The N-O and C=N stretching vibrations are at  $974$  and  $1604\text{ cm}^{-1}$ . In the spectra of the complexes, the C=N stretching vibrations of the oximes are shifted to the  $1595\text{--}1580\text{ cm}^{-1}$  range. These observations indicate the involvement of the nitrogen atom of the azomethine (C=N) group in the complexes<sup>23</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 (O-H...O) bending vibrations. Disappearance of the stretching vibrations of the (O-H) band which was present in the free ligand is further evidence for (O-H...O) band formation<sup>24</sup>.

**Table 2.** The Infrared Spectral<sup>a</sup> and Electronic Spectral Data for the Ligand and its Metal Complexes (cm<sup>-1</sup>).

Compound	$\nu$ (NH)	$\nu$ (CH <sub>2</sub> )	$\nu$ (CH=N-OH)	$\nu$ (M-N)	$\nu$ (M-O)	$\lambda_{max}$ ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )
CuL <sup>2</sup>	3178 m	2927 m	1596 s	511 w	451 w	637 (197), 459 (1.2x10 <sup>3</sup> ), 421 (1.8x10 <sup>3</sup> ), 327 (3.7x10 <sup>3</sup> ), 336 (7.1x10 <sup>3</sup> ), 298 (3.6x10 <sup>4</sup> )
CoL <sup>2</sup>	3180 m	2923 m	1575 s	520 w	435 w	673 (124), 607 (325), 362 (2.6x10 <sup>3</sup> ), 314 (6.0x10 <sup>3</sup> ), 225 (3.2x10 <sup>4</sup> )
NiL <sup>2</sup>	3177 m	2929 m	1571 m	503 w	420 w	630 (115), 346 (2.8x10 <sup>3</sup> ), 321 (4.7x10 <sup>3</sup> ), 314 (5.8x10 <sup>4</sup> )
PdL <sup>2</sup>	3175 m	2921 m	1605 m	500 w	435 w	434 (1.3x10 <sup>3</sup> ), 367 (3.7x10 <sup>3</sup> ), 332 (5.3x10 <sup>3</sup> ), 238 (4.6x10 <sup>4</sup> )
VOL <sup>2</sup>	3178 m	2928 m	1600 s	491 w	427 w	794 (132), 538 (347), 442 (3.5x10 <sup>3</sup> ), 407 (6.8x10 <sup>3</sup> ), 372 (3.7x10 <sup>3</sup> ), 319 (9.6x10 <sup>3</sup> ), 213 (5.1x10 <sup>4</sup> )
ZnL <sup>2</sup>	3172 m	2927 m	1573 m	504 w	423 w	427 (4.8x10 <sup>3</sup> ), 360 (2.4x10 <sup>3</sup> ), 314 (7.1x10 <sup>3</sup> ),

a: br (broad), s (strong), m (medium), w (weak).

The electronic spectra of all compounds were recorded in EtOH. The wavelengths of the absorption maxima are given in Table 2. A clear analogy is evident among the results for all compounds. In the spectra of the ligands HL-HL<sup>2</sup>, the  $\pi$ - $\pi^*$  transitions in the range 301-210 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 457-314 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>25</sup>. In the complexes, lower energy transitions can also be observed in the 794-618 nm range corresponding to the d-d transitions. In the spectrum of the Cu(II) complex, the d-d transition is observed in the 637 nm. This value is of particular importance since this was highly dependent on the geometry of the molecule. It is known that the transitions from a square-planar structure to a deformed tetrahedral structure lead to a red shift of absorption in the electronic spectra<sup>26</sup>. Thus, the smaller the value of the wavelength of the band corresponding to the transitions, the greater the resemblance between the geometry of the complex and that of the square-planar complex. Consequently, the larger the value of the ligand HL<sup>2</sup>, the more the geometry resembles that of a deformed tetrahedral structure.

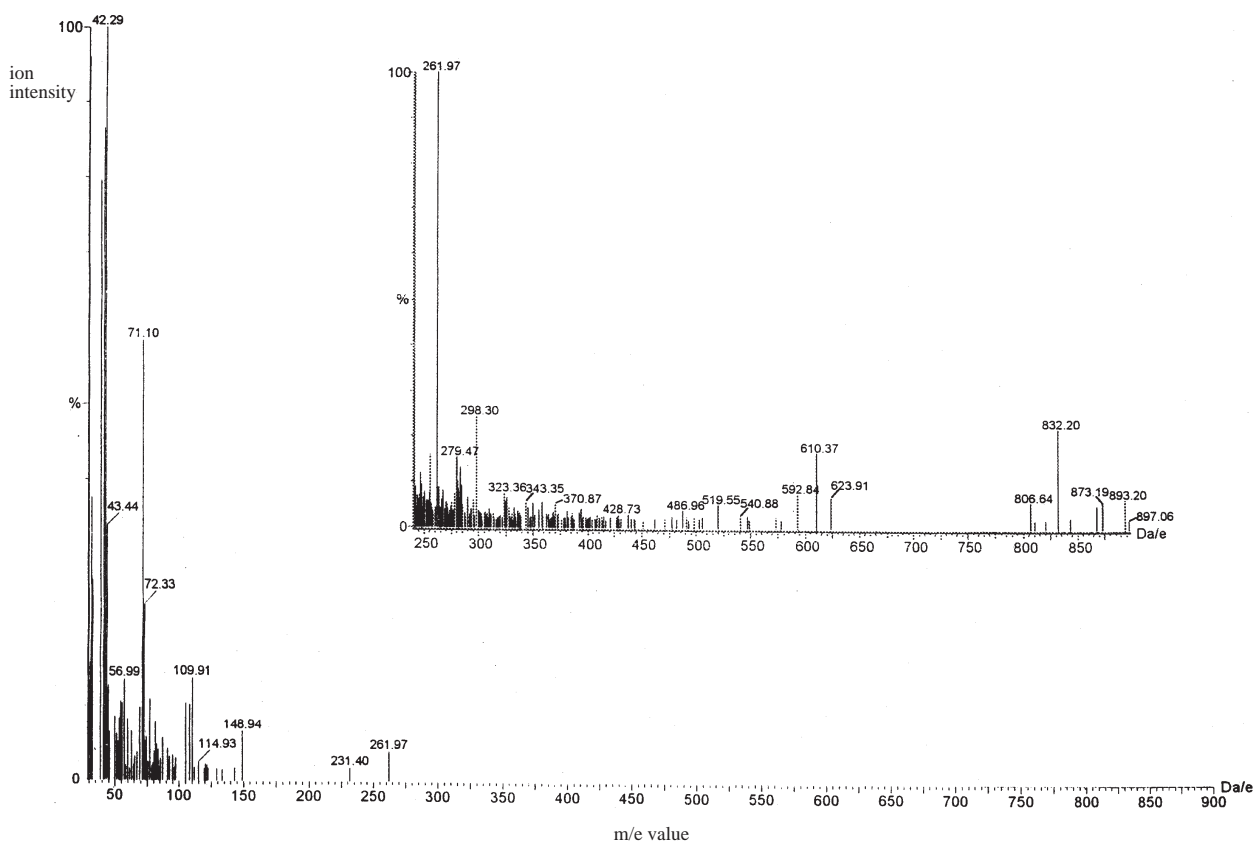
The magnetic moments (as B.M.) of the complexes were measured at room temperature. The structures of the monomeric complexes are supported by magnetic moment data. The Co(II) complex of the ligands HL<sup>2</sup> was found in paramagnetic character (4.47 B.M.) and tetrahedral geometry. The magnetic moment of the Cu(II) complex has a value in 1.77 B.M. and lies 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>27-29</sup>.

The magnetic moment of the VO(IV) complex is 1.78 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 complex of the VO(IV) may have the usual tetragonal pyramidal structure. The Ni(II), Pd(II) and Zn(II) complexes have diamagnetic character. The Ni(II) and Pd(II) complexes have square-planar geometry and the Zn(II) complex is of tetrahedral nature around the metal ion.

Additional structural information can be deduced from the <sup>1</sup>H- and <sup>13</sup>C-nmr spectra. A summary of the <sup>1</sup>H- and <sup>13</sup>C-chemical shifts for the Schiff base ligand, *vic*-dioxime and Ni(II), Pd(II) and Zn(II) oxime complexes are given in the experimental section. In the spectra of the Schiff base ligand HL, the singlet at 8.3 ppm is attributed to the proton of the azomethine group. The protons of the benzene rings are observed in the 6.2-7.15 ppm range as a multiplet. In other words, the oxime ligand shows two different

signals due to the secondary amine groups: the triplets in the 4.7-4.5 ppm range may be assigned to the protons of the nitrogen atom of the  $-\text{CH}_2\text{-NH-}$  group. The NH proton can be identified very easily, because of the disappearances of the chemical shifts of protons on  $\text{D}_2\text{O}$  exchange. In the spectra of the diamagnetic complexes, this group is shifted to the 5.5-5.9 ppm range. In the spectrum of the ligand  $\text{HL}^2$ , the deuterium exchangeable protons of the  $=\text{N-OH}$  groups show a chemical shift in the 11.3-12.0 ppm range as a singlet, which indicates an (E,E)-structure for the vicinal dioxime<sup>30</sup>. In the spectra of the Ni(II), Pd(II) and Zn(II) complexes, deuterium is exchangeable, and intramolecular bridging O-H...O protons appear as a singlets in the 15.7-16.4 ppm range.

The proton-decoupled  $^{13}\text{C}$ -nmr spectra of the diamagnetic complexes which appear as a singlet in the 168.14-168.67 ppm range corresponding to the two *vic*-dioxime ligands present are equivalent 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 are subjects of considerable interest in the literature<sup>31</sup>. In addition, benzenoid rings are observed in the 112.35-155.74 ppm range<sup>32</sup>.



**Figure 1.** The mass spectrum of the complex  $\text{ZnL}^2$ .

The mass spectrum of the complex  $\text{ZnL}^2$  is given in Fig.1. The relatively small intensities of the molecular ion peaks,  $[\text{M}]^+$ , are indicative of the fragmentation of the compounds, and this may reflect the number of heteroatoms present in each structure. In the spectrum of the *vic*-dioxime ligand  $\text{HL}^2$  the molecular ion peak  $[\text{M}+1]^+$  was found at  $m/e$  386. The spectrum of the ligand  $\text{HL}^2$  shows a peak at  $m/e$  87 due to the loss of the  $[\text{C}_2\text{H}_3\text{N}_2\text{O}_2]^+$  group. In the spectrum of the same ligand, the highest intensity peak at



m/e 211 may be assigned to the  $[C_{13}H_{13}N_3]^{+2}$  ion. For Ni(II), Pd(II) and Zn(II) complexes, the molecular ion peaks  $[M]^+$  are observed at m/e 884, 980 and 898, respectively. In the complexes the highest intensity peak at m/e 261 can be assigned to the removal of the  $[C_{15}H_{11}N_5]^{+2}$  ion.

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