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Studies of Some New Binuclear Metal(Ii)Complexes

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ABSTRACT

The ligand, H_4L^o , H_4L^m and H_4L^p were obtained from the reaction of 1, 2-Bis (*o*-aminophenoxy) ethane, 1, 2-bis (*m*-aminophenoxy) ethane and 1, 2-bis (*p*-aminophenoxy)-ethane with 1-chloro-1, 2-dihydroximinopropane. The analytical data of $[Zn_2(H_3L^o)_2(OAc)_2].H_2O$, $[Zn_2(H_2L^m)_2(H_2O)_2].H_2O$ and $[Zn_2(H_3L^p)(OAc)_2].2H_2O$ complexes indicate 2:2 metal to ligand stoichiometry. The brown-yellow colour of the Zn (II) complexes of H_4L^o , H_4L^m and H_4L^p indicates that the ligands are in the (E, E)-form(anti form).

H NMR results:

Ligands H_4L , H_4L and H_4L along with their Zn (II) complexes have been characterized on the basis of H NMR spectral results in DMSO- d_6 . In the H NMR spectrum of H_4L^o , there are deuterium exchangeable four signals at 12.08, 11.36, 10.82 and 10.14 ppm, as singlets, due to the -OH protons. In the 1H NMR spectrum of H_4L^m , four signals are observed for the protons since the -OH protons of the oxime groups are non-equivalent. In H_4L^m , the chemical shifts of -OH protons are observed at about 11.92, 11.45, 10.89 and 10.07 ppm as singlets. In the 1H NMR spectrum of H_4L^p , since the -OH protons of oximes are non-equivalent in the (E, E)-form, four peaks were observed for the protons. In this ligand, chemical shifts of -OH protons were observed around at 10.75, 10.50, 10.38 and 10.25 ppm as singlets. The singlet of these ligands, which belong to -OH, disappear after the addition of D_2O . A single chemical shift for the -OH proton indicates that the oxime groups prevail in the anti form.

KEYWORDS:

- *o*-aminophenoxy
- *m*-aminophenoxy
- *p*-aminophenoxy
- Zn (II) complexes
- DMSO- d_6

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INTRODUCTION

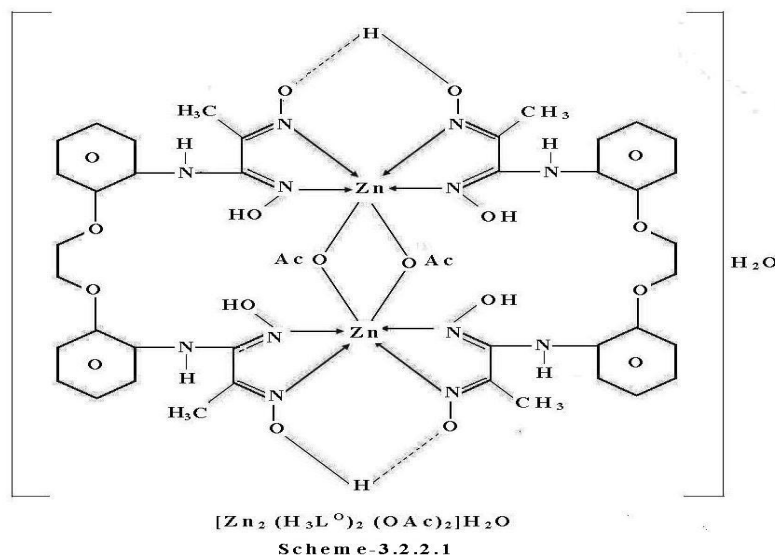
In coordination chemistry, Schiff bases have a significant role as ligands still a century after their discovery. The importance of Schiff bases and their metal complexes are important owing to their biochemical, electrochemical, analytical, antifungal, antibacterial activities and redox catalysts. Schiff bases with NO donors have structural similarities with natural biological systems and imports in elucidating the mechanism of transformation and racemisation reaction in biological systems due to presence of imine ($-N = CH-$) group, also the presence of nitrogen and oxygen donor atoms tunes the properties of the complexes to a great extent as effective and stereo specific catalysts for oxidation, reduction and hydrolysis, 2-Hydroxy Schiff bases and their metal complexes have been extensively studied and exhibit wide applications, especially in biological systems. The studies on binuclear metal complexes in which the two metal centres are held in close proximity have addressed ligand environment, redox behaviour, magnetic exchange interactions and spectroscopic properties; therefore these kinds of complexes still continue to play a very important role in our understanding of various aspects of coordination chemistry of metal. Also binuclear Schiff bases complexes have been found to be better catalysts than the mononuclear Schiff base complexes. The present situation, as described above in the field of research of metal (II) coordination compounds, has prompted us to undertake a programme of work to synthesize and characterize a series of new novel Schiff bases derived by condensing 1, 2-bis (*o/m/p*-aminophenoxy) ethane with 1, 2-dihydroximino -1-chloropropane along with binuclear zinc complexes.

MATERIALS AND METHODS

All reagents and chemical purchased from Aldrich-sigma were of analytical/spectroscopic grade and were used without further purification, Chemicals and solvents used for the preparation of Schiff base ligands and zinc (II) complexes are: 1, 2-Bis(*o*-aminophenoxy) ethane, 1, 2-bis(*m*-aminophenoxy) ethane, 1, 2-bis(*p*-aminophenoxy) ethane, 1, 2-dihydroximino 1-chloropropane⁷, zinc acetate, ethanol, diethyl ether, DMSO, DMF, acetone, ethyl acetate and chloroform. 1, 2 – Bis(*o/m/p*aminophenoxy) ethane have been prepared as per literature procedure¹⁻⁶ and reaction can be shown as follows:-

Synthesis of zinc (II) complexes:-

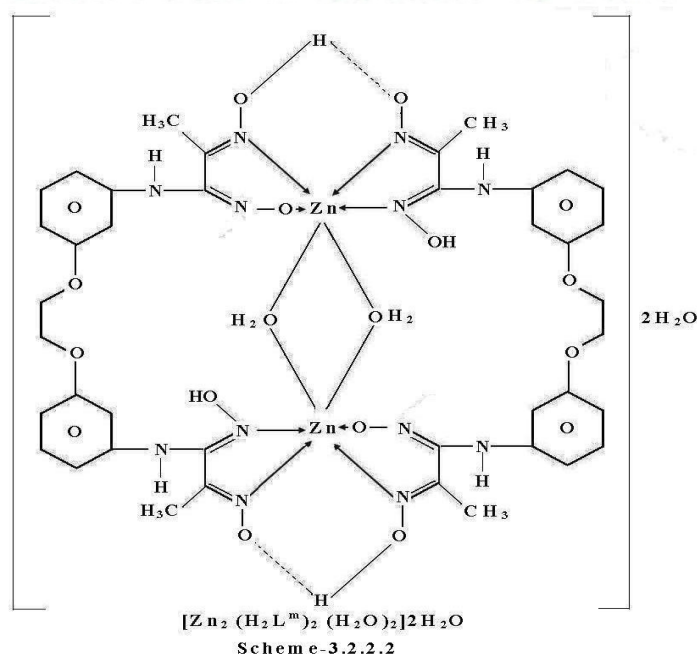
Synthesis of $[\text{Zn}_2 (\text{H}_3\text{L}^{\text{O}})_2 (\text{OAc})_2] \cdot \text{H}_2\text{O}$



The ligand $\text{H}_4\text{L}^{\text{O}}$ (0.35g, 0.40 mmol) was dissolved in absolute ethanol (5mL). Solutions of $\text{Zn}(\text{OAc})_2$ (0.07g, 0.40mmol) in ethanol (5mL) was added drop wise to the ligand solution with continuous stirring at 50°C . The colour of the solution immediately changed. The reaction mixture was stirred at this temperature for 2h and filtered and the precipitate was washed with water, ethanol and diethyl ether and finally dried in vacuum at 60°C^{8-10} . It was analysed as $\text{Zn}_2 (\text{C}_{44}\text{H}_{52}\text{N}_{12}\text{O}_{17})$ to give analytical results as follow:

Elements	Found%	Calculated%
Zinc	11.32	11.34
Carbon	45.62	45.80
Hydrogen	4.49	4.50
Nitrogen	14.50	14.57

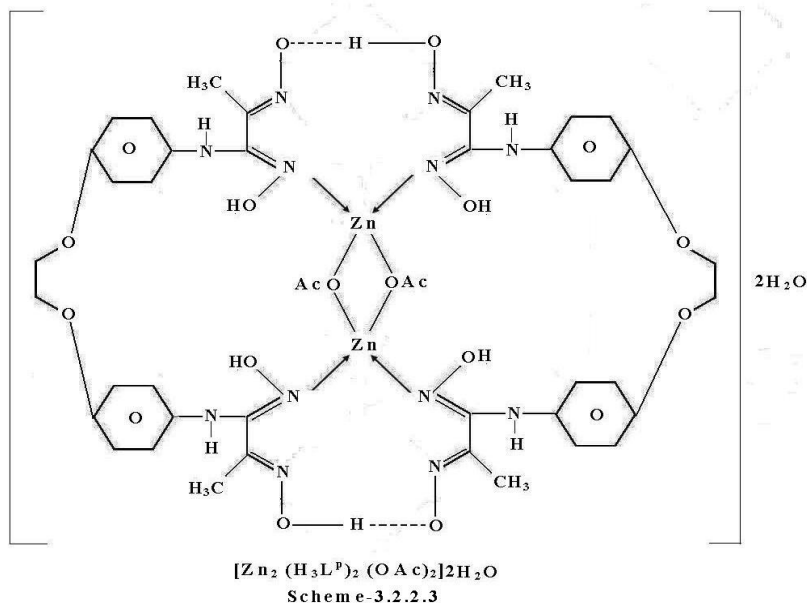
Synthesis of $[\text{Zn}_2 (\text{H}_2\text{L}^{\text{m}})_2 (\text{H}_2\text{O})_2] 2\text{H}_2\text{O}$



The ligand $\text{H}_4\text{L}^{\text{m}}$ (0.35g, 0.40 mmol) was dissolved in absolute ethanol (5mL). Solutions of $\text{Zn}(\text{OAc})_2$ (0.07g, 0.40mmol) in ethanol (5mL) was added drop wise to the ligand solution with continuous stirring at 50°C . The colour of the solution immediately changed. The reaction mixture was stirred at this temperature for 2h and filtered and the precipitate was washed with water, ethanol and diethyl ether and finally dried in vacuum at 60°C^{8-10} . It was analysed as $\text{Zn}_2 (\text{C}_{40}\text{H}_{52}\text{N}_{12}\text{O}_{18})$ to give analytical results as follow;

Elements	Found%	Calculated%
Zinc	11.65	11.67
Carbon	42.78	42.82
Hydrogen	4.61	4.63
Nitrogen	14.96	14.98

Synthesis of $[\text{Zn}_2 (\text{H}_3\text{L}^p)_2 (\text{OAc})_2] \cdot 2\text{H}_2\text{O}$



0.40mmol) in ethanol (5mL) was added drop wise to the ligand solution with continuous stirring at 50°C. The colour of the solution immediately changed. The reaction mixture was stirred at this temperature for 2h and filtered and the precipitate was washed with water, ethanol and diethyl ether and finally dried in vacuum at 60 °C. It was analysed as Zn_2 ($\text{C}_{44}\text{H}_{54}\text{N}_{12}\text{O}_{18}$) to give analytical results as follow;

Elements	Found%	Calculated%
Zinc	11.02	11.17
Carbon	44.92	45.09
Hydrogen	4.59	4.61
Nitrogen	14.20	14.35

Elemental analyses (C, H, N) were performed on a Leco932 CHNS-O elemental analyses apparatus. IR spectra were recorded on a Perkin-Elmer precisely spectrum one spectrometer as KBr pellets. ^1H NMR spectra were recorded on Bruker GmbH DPX-300 MHz high performance digital FT-NMR spectrometers ($\text{DMSO}-d_6$). Electronic spectra were obtained on a Shimadzu UV-1700 spectrometer. Magnetic susceptibilities were determined on a Sherwood scientific magnetic susceptibility diamagnetic corrections were calculated from Pascal's constants¹¹. Melting points were determined on a Gallenkamp melting points apparatus TGA and DTA curves were recorded on a Shimadzu DTG-60AH and DSC-60A thermo balance, respectively.

RESULTS AND DISCUSSION

The ligand, H_4L^o , H_4L^m and H_4L^p were obtained from the reaction of 1, 2-Bis (oamino-phenoxy) ethane, 1, 2-bis (*m*-aminophenoxy) ethane and 1, 2-bis (*p*-aminophenoxy)-ethane with 1-chloro-1, 2-dihydroximinopropane. The analytical data of $[Zn_2(H_3L^o)_2(OAc)_2].H_2O$, $[Zn_2(H_2L^m)_2(H_2O)_2].H_2O$ and $[Zn_2(H_3L^p)(OAc)_2].2H_2O$ complexes indicate 2:2 metal to ligand stoichiometry. Additional analytical data are given in Table.

ANAYTICAL AND PHYSICAL DATA ON LIGANDS AND Zn (II) COMPLEXES

Compounds	Empirical formula	f.w. g/mol	Colour	m.p. ^o C	Yield (%)	Elemental analysis (%)			
						Zn	C	H	N
H_4L^0	$C_{20}H_{24}N_6O_6$	444	Light Yellow	125	73.55	-	53.98 (54.05)	5.38 (5.40)	18.86 (18.92)
$[Zn_2 (H_3L^0)_2(OAc)_2] \cdot H_2O$	$Zn_2C_{44}H_{52}N_{12}O_{17}$	1152.80	Dark Yellow	300 ^d	70.53	11.32 (11.34)	45.62 (45.80)	4.47 (4.50)	14.55 (14.57)
H_4L^m	$C_{20}H_{24}N_6O_6$	444	Dark Yellow	110	82.77	-	53.97 (54.05)	5.36 (5.40)	18.88 (18.92)
$[Zn_2 (H_2L^m)_2(H_2O)_2] \cdot 2H_2O$	$Zn_2C_{40}H_{52}N_{12}O_{18}$	1120.08	Yellow	290 ^d	51.22	11.65 (11.67)	42.78 (42.82)	4.60 (4.63)	14.94 (14.98)
H_4L^p	$C_{20}H_{24}N_6O_6$	444	Brown	150	59.80	-	53.96 (54.05)	5.37 (5.40)	18.87 (18.92)
$[Zn_2 (H_3L^p)_2(OAc)_2] \cdot 2H_2O$	$Zn_2C_{44}H_{54}N_{12}O_{18}$	1170.8	Light Brown	300 ^d	78.49	11.02 (11.17)	44.92 (45.09)	4.58 (4.61)	14.20 (14.35)

d: decomposition.

H NMR results:

The ^1H NMR spectral results obtained for $\text{H}_4\text{L}^{\text{o}}$, $\text{H}_4\text{L}^{\text{m}}$ and $\text{H}_4\text{L}^{\text{p}}$ with their Zn (II) complexes in DMSO-d_6 , together the assignments, are given in Table. In the ^1H NMR spectrum of $\text{H}_4\text{L}^{\text{o}}$, there are deuterium exchangeable four signals at 12.08, 11.36, 10.82 and 10.14 ppm, as singlets, due to the –OH protons. In the ^1H NMR spectrum of $\text{H}_4\text{L}^{\text{m}}$, four signals are observed for the protons since the –OH protons of the oxime groups are nonequivalent⁴⁻⁶. In $\text{H}_4\text{L}^{\text{m}}$, the chemical shifts of –OH protons are observed at about 11.92, 11.45, 10.89 and 10.07 ppm as singlets. In the ^1H NMR spectrum of $\text{H}_4\text{L}^{\text{p}}$, since the –OH protons of oximes are non-equivalent in the (E, E)-form, four peaks were observed for the protons¹⁻³. In this ligand, chemical shifts of –OH protons were observed around at 10.75, 10.50, 10.38 and 10.25 ppm as singlets. The singlets of these ligands, which belong to –OH, disappear after the addition of D_2O . A single chemical shift for the –OH proton indicates that the oxime groups prevail in the anti-form¹⁻³. In ^1H NMR spectra of $\text{H}_4\text{L}^{\text{o}}$, $\text{H}_4\text{L}^{\text{m}}$ and $\text{H}_4\text{L}^{\text{p}}$ the deuterium exchangeable protons of NH group appear as singlets at $\delta=6.44$ and 6.19 ppm for $\text{H}_4\text{L}^{\text{o}}$, at $\delta=6.49$ and 6.11 ppm for $\text{H}_4\text{L}^{\text{m}}$, at $\delta=5.75$ and 5.44 ppm for $\text{H}_4\text{L}^{\text{p}}$.

In the ^1H NMR spectrum of $[\text{Zn}_2(\text{H}_3\text{L}^{\text{o}})_2(\text{OAc})_2]\cdot\text{H}_2\text{O}$, $[\text{Zn}_2(\text{H}_2\text{L}^{\text{m}})_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ and $[\text{Zn}_2(\text{H}_3\text{L}^{\text{p}})_2(\text{OAc})_2]\cdot 2\text{H}_2\text{O}$, only slight differences between those of the ligands ($\text{H}_4\text{L}^{\text{o}}$, $\text{H}_4\text{L}^{\text{m}}$ and $\text{H}_4\text{L}^{\text{p}}$) and their Zn (II) complexes were observed while the chemical shift of D_2O exchangeable NH protons were observed at $\delta=6.63$ and 6.49 ppm, as doublets, for $[\text{Zn}_2(\text{H}_3\text{L}^{\text{o}})_2(\text{OAc})_2]\cdot\text{H}_2\text{O}$, at $\delta=6.58$ and 6.41 ppm, as doublets, for $[\text{Zn}_2(\text{H}_2\text{L}^{\text{m}})_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ and at $\delta=6.73$, 6.550, 6.33 and 6.49 ppm, as singlet's.

Table-4.2
¹H NMR SPECTRA OF THE LIGANDS (H₄L^o, H₄L^m AND H₄L^p) AND THEIR Zn (II)

Compounds	OH ^a	C-CH ₃	HC=N	Ar-CH	N-H	O-CH ₂	O-H ^o ...O
H ₄ L ^o	12.08, 1136, 1082, 1014 (4H, s)	9.0 (12H, s)	8.54, 8.13 (2H, s)	7.21-6.67 (8H, m)	6.44, 6.19 (2H, s)	4.72-1.12 (4H, m)	-
[Zn ₂ (H ₃ L ^o) ₂ (OAc) ₂].2H ₂ O	112, 1147, 10.90, 1070 (4H, s)	9.1 (12H, s)	8.80, 8.33, 8.10, 7.75 (4H, s)	7.30-6.70 (16H, m)	6.63, 6.49 (4H, d)	4.70-1.18 (8H, m)	15.31 (2H, s)
H ₄ L ^m	11.92, 11.45, 10.89, 10.07, (4H, s)	9.2 (12H, s)	8.27, 7.96 (2H, s)	7.32-6.76 (8H, m)	6.49, 6.11 (2H, s)	4.27-1.18 (4H, m)	-
[Zn ₂ (H ₃ L ^m) ₂ (H ₂ O) ₂].2H ₂ O	11.78, 10.70, (2H, s)	9.0 (12H, s)	8.89, 8.45, 7.78, 7.50 (4H, s)	7.27-6.68 (16H, m)	6.58, 6.41 (4H, d)	4.23-1.07 (8H, m)	18.11 (2H, s)
H ₄ L ^p	10.75, 1050, 10.38, 10.90 (4H, s)	9.1 (12H, s)	8.75, 8.31 (2H, s)	7.12-6.50 (8H, m)	5.75, 5.44 (2H, s)	4.62-1.12 (4H, m)	-
[Zn ₂ (H ₃ L ^p) ₂ (OAc) ₂].2H ₂ O	11.85, 10.85, 10.38, 10.04 (4H, s)	9.0 (12H, s)	8.38, 8.23, 8.12, 7.92 (4H, s)	7.68-7.25 (16H, m)	6.73, 6.50, 6.33, 5.69 (4H, s)	4.49-1.10 (8H, m)	14.99 (2H, s)

a: Deuterium exchangeable.

IR Results:

The characteristic infrared spectrum data are given in Table and representative spectrum of one of the ligand H₄L^o and its Zn (II) complexes is shown in figs.

The broad bands within the range 3423-3247 cm⁻¹ for H₄L^o, 3370-3203 cm⁻¹ for H₄L^m and 3400-3208 cm⁻¹ H₄L^p can be attributed to stretching vibrations of free ν (OHNH) and intermolecular H-bonding. The observed negative shift of ν (C=N) stretching in the IR spectra of [Zn₂(H_yL^x)₂X₂].nH₂O complexes (x: o, m and p; y=3, 2, 3; X: OAc, H₂O and OAc; n: 1, 2 and 2,

respectively) 1599, 1596 and 1641-1604 cm^{-1} , respectively, relative to free H_4L^x ligands 1615, 1593 and 1670 cm^{-1} . Respectively, indicates the participation of the azomethine nitrogen and/or oxygen atoms of ligands in coordination with the Zn (II) ion. The IR spectra of $[\text{Zn}_2(\text{H}_2\text{L}^x)_2\text{X}_2] \cdot n\text{H}_2\text{O}$ metal complexes were characterized by the appearance of significant absorption bands in the region 1690, 1684 and 1739 cm^{-1} , respectively, due to $\nu(\text{O}-\text{H} \cdots \text{O})$ ⁹.

CHARACTERISTIC IR BANDS (IN KBr, cm^{-1}) OF LIGANDS (H_4L^0 , H_4L^m AND H_4L^p) AND THEIR Zn (II) COMPLEXES								
Compounds	$\nu(\text{H}_2\text{O}/\text{OH})$	$\nu(\text{N-H})$	$\nu(\text{O}-\text{H} \cdots \text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N-O})$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\nu(\text{M}-\text{H}_2\text{O})$
H_4L^0	3370	3247	-	1615	1053	-	-	-
$[\text{Zn}_2(\text{H}_3\text{L}^0)_2(\text{OAc})_2] \cdot \text{H}_2\text{O}$	3360	3376	1638	1599	1055	1536	1347	-
H_4L^m	3375	3060	-	1603	1074	-	-	-
$[\text{Zn}_2(\text{H}_3\text{L}^m)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	3323	3060	1634	1585	1077	-	-	847
H_4L^p	3385	3208	-	1570	1067	-	-	-
$[\text{Zn}_2(\text{H}_3\text{L}^p)_2(\text{OAc})_2] \cdot 2\text{H}_2\text{O}$	3390	3197	1680	1641-1604	1062	1552	1367	-

s: symmetric, as: asymmetric.

The broad bands within the range $3423\text{--}3247\text{ cm}^{-1}$ for $\text{H}_4\text{L}^{\text{o}}$, $3370\text{--}3203\text{ cm}^{-1}$ for $\text{H}_4\text{L}^{\text{m}}$ and $3400\text{--}3208\text{ cm}^{-1}$ $\text{H}_4\text{L}^{\text{p}}$ can be attributed to stretching vibrations of free ν (OHNH) and intermolecular H-bonding. The observed negative shift of ν (C=N) stretching in the IR spectra of $[\text{Zn}_2(\text{H}_y\text{L}^{\text{x}})_2\text{X}_2]\text{nH}_2\text{O}$ complexes (x: o, m and p; y=3, 2, 3; X: OAc, H_2O and OAc; n: 1, 2 and 2, respectively) 1599 , 1596 and $1641\text{--}1604\text{ cm}^{-1}$, respectively, relative to free $\text{H}_4\text{L}^{\text{x}}$ ligands 1615 , 1593 and 1670 cm^{-1} . Respectively, indicates the participation of the azomethine nitrogen and/or oxygen atoms of ligands in coordination with the Zn (II) ion. The IR spectra of $[\text{Zn}_2(\text{H}_2\text{L}^{\text{x}})_2\text{X}_2]\text{nH}_2\text{O}$ metal complexes were characterized by the appearance of significant absorption bands in the region 1690 , 1684 and 1739 cm^{-1} , respectively, due to $\nu(\text{O-H}\cdots\text{O})^9$. A sharp band observed between $1078\text{--}1053\text{ cm}^{-1}$ in ligands and Zn (II) complexes are assigned to the ν (N-O) vibration. The shifts of N-O absorbance to lower energy are consistent with the protonation occurring at the hydrogen-bridged oxime oxygen atoms, yielding a covalent O-H bond. The formation of O-H bands results in the removal of electron density from N-O bond and corresponding increase in the N-O bond length and decreased NO stretching vibration¹⁰. The ν (O-H) stretching band observed at 3423 , 3370 and 3400 cm^{-1} in the IR spectrum of $\text{H}_4\text{L}^{\text{o}}$, $\text{H}_4\text{L}^{\text{m}}$ and $\text{H}_4\text{L}^{\text{p}}$, respectively, together with the existence of a H-bridge ν (N-O) stretching in the IR spectra of the $[\text{Zn}_2(\text{H}_3\text{L}^{\text{o}})_2(\text{OAc})_2]\text{H}_2\text{O}$, $[\text{Zn}_2(\text{H}_2\text{L}^{\text{m}})_2(\text{H}_2\text{O})_2]\text{2H}_2\text{O}$ and $[\text{Zn}_2(\text{H}_3\text{L}^{\text{p}})_2(\text{OAc})_2]\text{2H}_2\text{O}$ complexes provide support for MN_4O_2 -type, MN_3O_3 -type and MN_2O_2 -type coordination in the complexes, respectively.

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