

Synthesis and Characterization of New Tetraazamacrocyclic Ligand and their Complexes with $\text{Co}^{(\text{II})}$, $\text{Zn}^{(\text{II})}$, $\text{Cd}^{(\text{II})}$, $\text{Re}^{(\text{V})}$

By

Jenan M. Mahmood

Diyala University/ College of Science /Department of Chemistry

Abstract

A diethyl phthalate was reacted with 1,2-diaminoethane to produce the new tetradentate macrocyclic ligand [1,4,13, 16- tetraazacyclo (6,11- 18,23) tetracos- (6,8,10(11),18,20,22(23)- hexane- 5,12,17,24- tetra one] (H_4L). The reaction of this ligand with $[\text{ReOCl}_3(\text{pph}_3)_2]$ resulted in new trans-dioxo rhenium (V) complex of the general formula $[\text{ReO}_2(\text{L})]^{-3}$. Also the work includes the reaction of some metal ions with this ligand, and complexes of the general formula $[\text{M}(\text{H}_n\text{L})\text{X}]^{-m}$ (where: $\text{M}=\text{Co}^{(\text{II})}$, $n= 1$, $x=\text{Cl}_2$, $m= 3$; $\text{M}=\text{Zn}^{(\text{II})}, \text{Cd}^{(\text{II})}$, $n= 0$, $x= 0$, $m=2$) were prepared. All compounds have been characterized as needed by spectroscopic methods [IR, UV-Vis and Atomic absorption], microanalysis (C.H.N) along with conductivity measurements. The above studies show the geometry around Zn^{+2} and Cd^{+2} ions is tetrahedral structure, while the Co^{+2} and Re^{+5} complexes are forming octahedral structure.

Introduction

The chemistry of macrocyclic ligands and their complexes have attracted the interest of both inorganic and bioinorganic chemists in recent years⁽¹⁻³⁾ due to their unique structural properties and biological activities⁽⁴⁾. Although essential metals carry out important biological functions because they act as cofactors for a wide variety of metalloproteins and enzymes⁽⁵⁾. Recently there have been many investigations of the synthesis, structures and properties of various types of N-functionalized tetraaza macrocyclic ligands and their transition metal complexes⁽⁶⁾. Cobalt is a relatively rare element of the earth's crust, which is essential to mammals in the form of cobalamin (Vitamin B₁₂)⁽⁷⁾. In the present study was undertaken to compare the structure and solution chemistry of related rhenium complexes to these structurally characterized technetium species such studies are also of concern to nuclear medicine⁽⁸⁻⁹⁾. Macrocyclic polyamine ligands their metal complexes containing axial ligands are important because of their structure and chemical properties, which are often quite different from those of uncoordinated axial groups⁽¹⁰⁻¹¹⁾. This paper reports the synthesis and characterization of new tetradentate ligand type N₄ derived from the reaction of (1,2-diaminoethane and diethyl phthalate and its complexes with Co(II), Zn(II), Cd(II) and Re(V).

Experimental

Reagents were purchased from Fluka, Riedel – Dehaen, Hopkins and Williams and Merck Chemical Co. I.R. spectra were recorded as (KBr) or (CsI) discs using Pye- Unicam -Sp3-300 in the range (4000-200)cm⁻¹. Electronic spectra of the all preparation compounds were measured in the region (200-700) nm for 10⁻³ M solution in (H₂O) at 25 °C using Shimadzu UV-1650 PC Ultra Violet –visible Spectrophotometer with (1) cm matched quartz cell. Elemental microanalysis were performed using (C.H.N) analyser, model 240 B(Perkin Elmer). While metal contents of the complexes were determined by atomic absorption (A.A) Technique using a Shimadzu AA-680G atomic absorption spectrophotometer. Electrical molar conductivity measurements of the complexes were recorded at 25°C for 10⁻³ M solution of the samples in (H₂O) using a Wiss-Techn. Werkstätten. D812 Weilheim.

Synthesis of the ligand (H₄L)

A solution of [1,2-diaminoethan(2×10^{-3} mole) in methanol (30ml)] was added slowly with stirring to a mixture of [diethyl phthalate (2×10^{-3} mole) dissolved in methanol (30 ml)] The mixture was allowed to reflux for 3 hours under nitrogen blanket, then cooled to room temperature, after cooling , 5 ml of concentrated hydrochloric acid was added with stirring to reaction mixture, and continued at room temperature for 30 min. A white solid precipitate formed which was filtered, washed with diethyl ether and air dried to give (H₄L) as a white solid, yield (60%).

Synthesis of [ReOCl₃(pph₃)₂]

To prepare the complex, (100 ml) round bottomed flask in which (1 gm, 5.4×10^{-4} M) of Rhenium metal was inserted in ice bath and (16 ml) of hydrogen peroxide, (35%) was added gradually with continuous stirring, after complete the liquid was evaporated from the reaction mixture nearly to dryness using a water bath. Then the flask was inserted again in the ice bath and mixture of (10 ml of hydrochloric acid 37% and 10gm, 3.8×10^{-3} M of triphenylphosphine) dissolved in (50 ml) of acetone was added gradually again with stirring to form greenish yellow precipitate. The mixture was then refluxed for 90 minutes and then left for an hour to cool. It was then filtered and washed with (10 ml) of ethanol and left for dryness giving the final greenish yellow precipitate with a weight of (4.4 gm) and (98%) efficiency.

Synthesis of complexes

A(100 ml) round bottom flask was charged with [(5×10^{-4} mole) H₄L and triethyl amine Et₃N(2×10^{-2} mole) dissolved in (25 ml)methanol]. A solution of [CoCl₂.6H₂O (5×10^{-3} mole) in (15 ml) methanol] was added dropwise with stirring to the above solution. The reaction mixture was refluxed for 1 hour under inert atmosphere of nitrogen gas. The white precipitate formed was collected by filtration, washed with dry diethyl ether (6 ml) and dried at room temperature to give (63%) yield of the title complex. All complexes as a similar method mentioned in preparation of Co(II) complex was used to prepare the complexes of (H₄L) with (Zn^(II), Cd^(II) and Re^(V)) ions by using chloride salts for Zn^(II), Cd^(II), and [ReOCl₃(pph₃)₂] . Table(1) stated the quantities, reaction conditions and physical properties of the ligand and prepared complexes.

Results and Discussion

Synthesis of the Ligand(H₄L)

The (H₄L) which molecular formula is (C₂₀H₂₀N₄O₄), was prepared by the reaction of diethyl phthalate with 1,2-diaminoethan in methanol solvent, according to the general method shown in scheme-1. The ligand was characterized by elemental analysis (table-2), I.R. spectra (table -3) and UV-Vis spectra (table-4) , IR spectrum of the ligand, (Fig.1) displays a band at (3050)cm⁻¹ due to ν (N-H) stretching frequency⁽¹²⁾. The two band at (1200) , (1230)cm⁻¹ have been assigned to ν (C-N) stretching frequency⁽¹³⁾. In addition to these bands, band at (1610) cm⁻¹ appears in the spectrum of (H₄L) assigned to ν (C=O) amide stretching Vibration⁽¹⁴⁾, and a new bend at (1100) cm⁻¹ due to formation of macrocycle⁽¹⁵⁾. While UV-Vis spectrum (Fig.3) exhibits a high intense absorption peak at (225 nm, 44444 cm⁻¹, ϵ_{\max} =1854 M⁻¹ . cm⁻¹) due to ($\pi \rightarrow \pi^*$) electronic transition ,and two absorption peak at(248 nm, 40323 cm⁻¹, ϵ_{\max} =909 M⁻¹ ,cm⁻¹), (254 nm, 39370 cm⁻¹, ϵ_{\max} =533M⁻¹ , cm⁻¹ are attributed to ($n \rightarrow \pi^*$) electronic transition.^(12,16)

Synthesis of Complexes

All complexes were prepared by a similar method, shown in scheme (2). From the reaction of the ligand (H₄L) with MCl₂. XH₂O (Where :M=CO^(II), Zn^(II) , Cd^(II)) and [ReOCl₃(pph₃)₂] were carried out in MeOH under reflux in the presence of triethyleamine. The complexes were stable in solution and electrolytes. The analytical and physical data (table- 1&2) and spectral data (table-3&4). All complexes dissolve in MeOH solvent.

IR. Spectra

The IR. Spectra for all complexes (table -3) revealed a medium band at range (1565-1622) cm⁻¹ due to ν (C=O) stretching frequency of amide group , which was shifted to lower frequency in comparison with that of free ligand (H₄L). The shifting in ν (C=O) can be related to the delocalization of metal ion electronic density in to π -orbital of the ligand(π -back bonding)⁽⁷⁾. The IR. Spectrum of the ligand exhibited a broad band at (3050)cm⁻¹ indicated to ν (N-H) vibration while in IR spectrum of Co^(II) complex this band was shifted to high frequency and appeared at 3200 cm⁻¹, but this band disappeared in IR. Spectrum of Zn^(II), Cd^(II) and Re^(V)

complexes, that is refer to all protons of four (N-H) group were removed and anionic ligand (-4) was formed in Zn^(II), Cd^(II) and Re^(V) complexes. The shifting and disappeared of the band (N-H) in all complexes may be a result to coordinate modes of metal ions through the nitrogen atoms of N-H group. Moreover the IR. spectra of the complexes show new band at range (360-545) cm⁻¹ due to $\nu(\text{M-N})$ vibration ⁽¹⁷⁾. Only [Co(HL)Cl₂]⁻³ spectrum (Fig. 2) shows a band at (430,360) cm⁻¹ which assigned to $\nu(\text{Co-N})$ ^(18,19), while Re(V) complex shows a characteristic band at (752) cm⁻¹ assigned to trans dioxo (O=Re=O) ⁽²⁰⁾.

Electronic Spectra

The electronic spectra of the free ligand (H₄L) and their complexes are summarized in (table-4). The UV-Vis spectra of the complexes displayed absorption peaks at range (225-280)nm assigned for ligand field which were shifted to high or low frequency when it comparison with spectrum of the free ligand (H₄L) ⁽²¹⁾. The electronic spectrum of the complexes [Zn(L)]⁻², [Cd(L)]⁻² and [ReO₂(L)]⁻³ exhibit a new absorption peak at (376)nm, (362)nm and (305)nm respectively, which are attributed to charge transfer (M→L)⁽²²⁾. In the [Co(HL)Cl₂]⁻³ complex the two peaks at (530)nm and (590)nm are attributed to (d-d) electronic transition type (⁴T_{1g}→⁴T_{1g(p)}) and (⁴T_{1g}→A_{2g}) respectively, suggesting octahedral geometry about Co(II)⁽²¹⁾. The UV-Vis spectra of [Zn(L)]⁻², [Cd(L)]⁻² complexes show no absorption peak in the range (300-700)nm, that is indicates no(d-d) electronic transition happened (d¹⁰-system) in the visible region that is a good result for Zn(II), Cd(II) tetrahedral Complexes ^(23,24,25). The electronic spectrum of [ReO₂(L)]⁻³ (Fig-3), shows a new absorption peak at (453)nm attributed to (d-d) electronic transition type (³T_{1g}→³T_{2g}), in fact this result is an a good agreement with the previous work of Re(V) complexes of octahedral geometry ^(9,26,27).

Molar Conductance

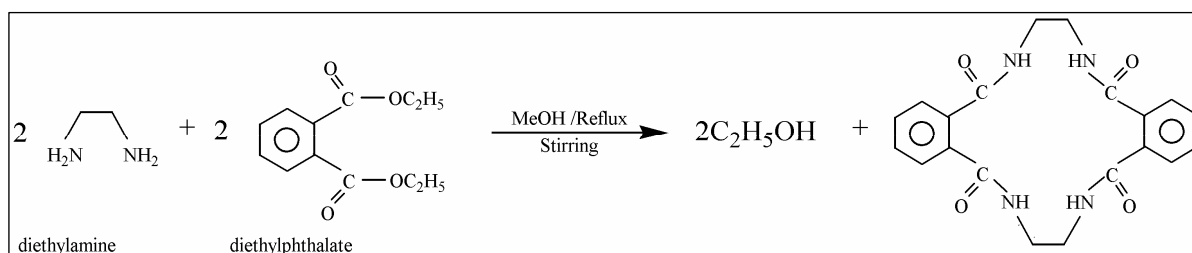
The molar Conductance of the complexes in H₂O solvent in 10⁻³ M at 298 k (table -2) indicated electrolytic nature with (3:1) ratio for [Co(II), Re(V)] and (2:1) ratio for [Zn(II), Cd(II)] complexes^(27, 28).

Atomic Absorption

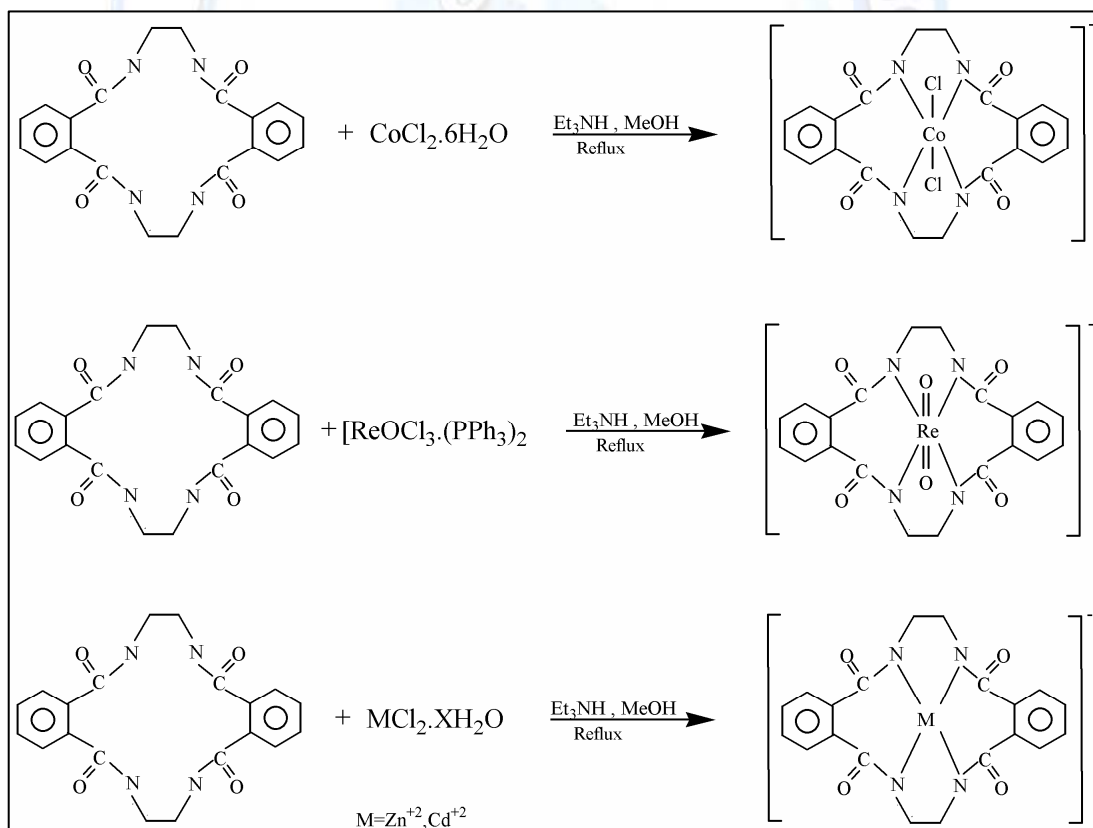
The atomic absorption measurements (table-2) for all complexes gave approximated values for its theoretical.

Conclusion

Our investigation this suggest that the ligand (H_4L) behaves as tetradentate on complexation with metals ion forming octahedrally coordinated about $[Co(II), Re(V)]$ ions and tetrahedrally coordinated about $[Zn(II), Cd(II)]$ ions



Scheme (1): Synthesis method of Ligand (H_4L)



Scheme (2) : Synthesis method of Complexes

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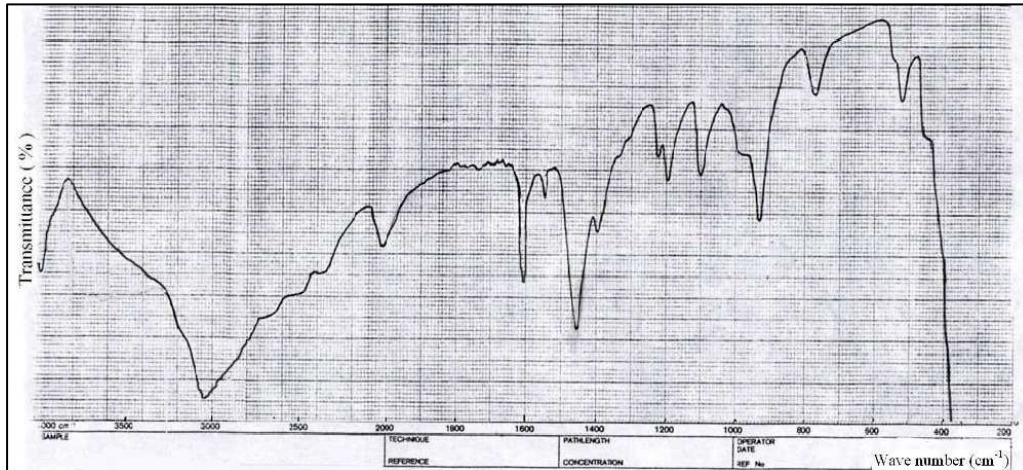


Figure (1) : IR spectrum of Ligand (H₄L)

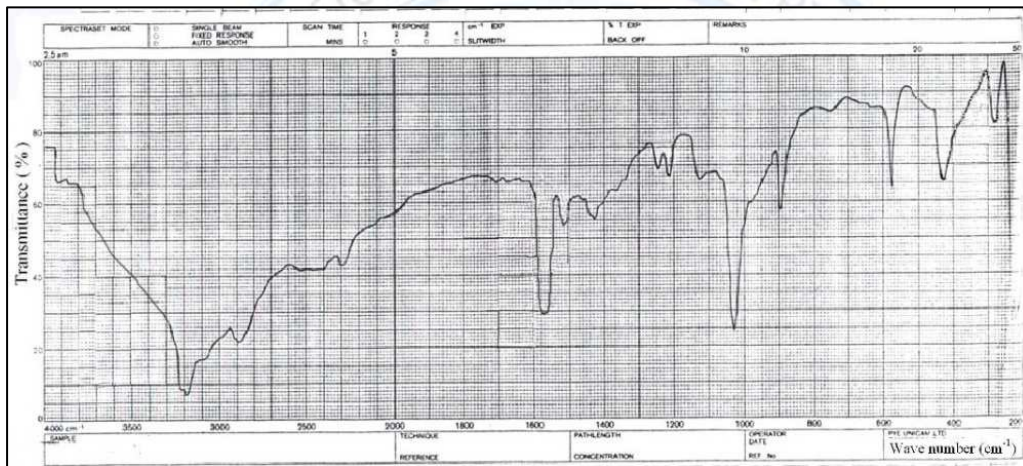


Figure (2): IR spectrum of Complex [Co (HL)Cl₂]⁻³

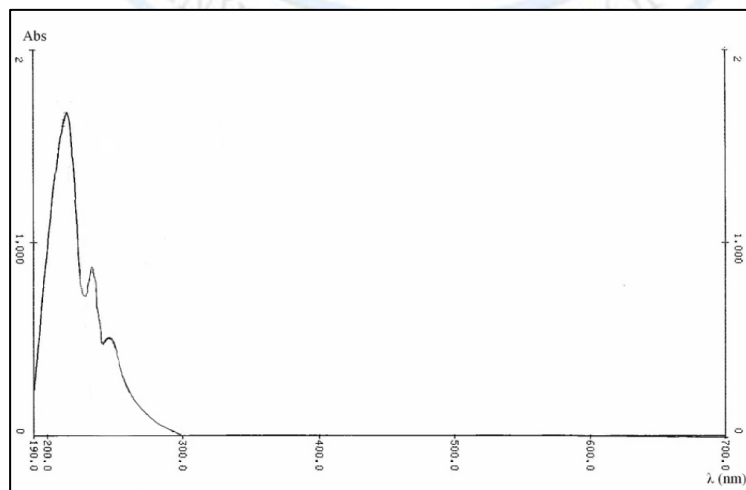


Figure (3): UV-Vis spectrum of Ligand (H₄L)

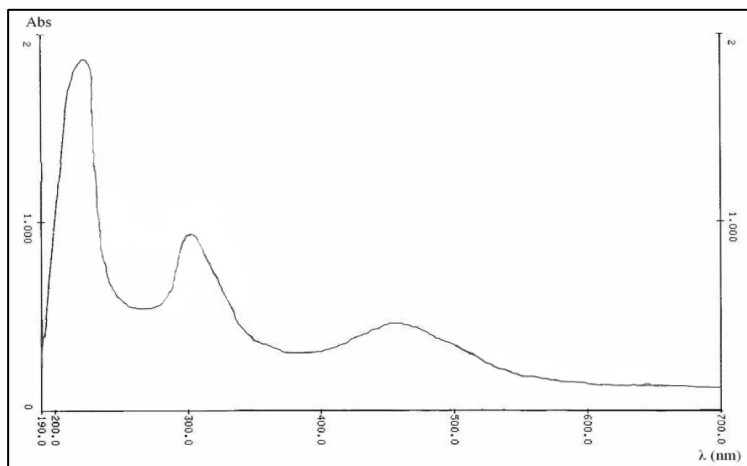
Figure (4) : UV-Vis spectrum of Complex $[(\text{ReO}_2(\text{L}))_3]^{-3}$

Table (1): Physical properties of the prepared compounds and weight of metal chloride salt used

Compound	Colour	Yield %	Reactent Metal salt	Weight of reactant metal salt(g) = 5×10^{-4} mole
(H ₄ L)	White	60	-----	-----
(Et ₃ NH) ₃ [Co(HL)Cl ₂]	Orange	63	CoCl ₂ .6H ₂ O	0.119
(Et ₃ NH) ₂ [Zn(L)]	White	55	ZnCl ₂	0.321
(Et ₃ NH) ₂ [Cd(L)]	White	85	CdCl ₂ .H ₂ O	0.345
(Et ₃ NH) ₃ [ReO ₂ (L)]	deep Yellow	72	[ReOCl ₃ (pph ₃) ₂]	0.416



Table (2): Result of elemental analysis and molar conductance of prepared compounds

Compound	M.wt	M.C*	Microanalysis Found % (Calcu)%			
			C	H	N	Metal
(H ₄ L)	380	(63.16)	(5.26)	(14.74)
			62.66	5.17	14.34
[Co(HL)Cl ₂] ⁻³	813	325	(57.09)	(7.99)	(12.05)	(7.26)
			55.58	7.79	11.62	6.73
[Zn(L)] ⁻²	643	220	(59.72)	(7.15)	(13.06)	(10.11)
			59.26	6.7	12.75	9.59
[Cd(L)] ⁻²	690.4	233	(55.62)	(6.66)	(12.17)	(16.28)
			55.06	6.2	11.86	15.73
[ReO ₂ (L)] ⁻³	872.2	305	(52.28)	(7.34)	(8.03)	(21.35)
			52.1	7.21	7.84	21.15

M.C*=Molar Conductance ohm⁻¹. cm². mol⁻¹

M.wt = Molecular weight

Table (3): I.R. Spectral data of the (H₄L) and its metal

Compound	ν (N-H)	ν (C=O)	δ(N-H)	ν (C-N)	Macracycle framework	ν (M-N)	Additional peaks
(H ₄ L)	3050	1610(m)	1550(w)	1200(w) 1230(w)	1100(w)	-----	1400 δ _s (CH ₂) 920,780,δ(C-H)arm 0.0.p 522δ (C≡C)arm 0.0.p
[Co(HL)Cl ₂] ⁻³	3200b	1565(m)	1520(W)	1240(w) 1210(w)	1030(st)	430(w) 360(w)	1430ν (C≡C)arm 895δ(C-H)arm 0.0.p 280 ν (Co -Cl)
[Zn(L)] ⁻²	-----	1620(m)	-----	1185(w) 1150(w)	1090(w)	540(w)	1440 ν (C≡C)arm 1390,δ _s (CH ₂) 920, 755, δ(C-H)arm 0.0.p

$[\text{Cd}(\text{L})]^{2-}$	_____	1622(m)	_____	1158(w)	1040(st)	545(w)	1475, ν ($\text{C}\equiv\text{C}$) arm 1410 δ_s (CH_2) 745, δ ($\text{C}\equiv\text{C}$) arm 0.0.p
$[\text{ReO}_2(\text{L})]^{3-}$	_____	1585(m)	_____	1220 1180	1100(w) 1040(w)	470(w) 435(w)	1465, ν ($\text{C}\equiv\text{C}$) arm 1380, δ_s (CH_2) 795, ν (ReO_2)

b = broad, st = strong, w = weak, m =medium, ν =stretching, δ =bending

Table (4): Electronic Spectral data of the (H_4L) and its metal complexes

Compound	λ (nm)	ν (cm-1)	ϵ_{max} (molar $^{-1}$ cm $^{-1}$)	Assignment	propose structure
(H_4L)	225	44444	1854	π - π^*	
	248	40323	909	n - π^*	
	254	39370	533		
$[\text{Co}(\text{HL})\text{Cl}_2]^{3-}$	280	35710	3840	ligand Field	octahedral
	530	18868	79	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{p})$	
	590	16949	58	${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$	
$[\text{Zn}(\text{L})]^{2-}$	265	37736	1800	ligand field	tetrahedral
	376	26596	2320	Charge transfer	
$[\text{Cd}(\text{L})]^{2-}$	260	38462	1696	ligand field	tetrahedral
	362	27778	2300	Charge transfer	
$[\text{ReO}_2(\text{L})]^{3-}$	233	42918	1896	ligand field	octahedral
	305	32787	1945	Charge transfer	
	453	22075	498	${}^3\text{T}_{1g} \rightarrow {}^3\text{T}_{2g}$	

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