

Synthesis and Structural Studies on some Transition Metal Complexes of Bis-(benzthiazole-2-thio) Ethane, Pyridine and Bis-(benzoxazole-2-thio) Ethane Ligands

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ABSTRACT

Transition metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) with the tetradentate ligands [$L^1=1,2$ -bis-(benzothiazol-2-thio)ethane, $L^2=1,2$ -bis-(benzoxazole-2-thio)ethane, $L^3=2,6$ -bis-(benzothiazole-2- io) pyridine], derived from the condensation of 2-mercaptobenzothiazole or 2-mercaptobenzoxazole and 1,2-dibromoethane or 2,6-dichloropyridine were synthesized. Characterization has been done on the basis of analytical conductance, magnetic data, infrared, electronic spectra for the ligands and X-Ray diffraction for L^2 . From analytical data the stoichiometry of the complexes has been found to be (1:1) (metal: ligand). IR spectra data suggest that the ligands behave as bidentate with S,S donor sequence toward the metal ions. On the basis of the above spectral, physicochemical, data as well as magnetic moment measurements tetrahedral geometries were assigned for the complexes.

Keywords: Metal complexes, benzothiazole-2-thio derivatives, benzoxazole-2-thio derivtives, spectral study.

INTRODUCTION

The chemistry of nitrogen-sulfur chelating ligands is more significant particularly by the discovery of the accuracy of similar donor environments in several bioactive molecules⁽¹⁻⁴⁾. The presence of sulphur in the ligand molecule does apparently improve the activity of the ligand. Similarly heterocyclic-N donor ligands are π -deficient molecule and their transition metal chemistry are also active area of current research. Benzothiazoles and Benzoxazoles are important moieties, they have found practical application in a number of fields endowed with variety of biological activities and have wide range of therapeutic properties^(5,6), of which the most potent is an antibiotic⁽⁷⁾, antibacterial⁽⁸⁾, antifungal⁽⁹⁾, antitumor⁽¹⁰⁾, anti-inflammatory⁽¹¹⁾, antitubercular⁽¹²⁾ activity. Therefore substituted benzothiazoles and benzoxazoles have attracted the interest of various research group, especially since it has been reported that the influence of the substitution at 1,2 and 5-positions is very important for their pharmacological effect⁽¹³⁾. Several groups have reported cobalt (II) and Zn(II) coordination compounds showing a similar stoichiometry $[M(bz)_2X_2]$ (M(II)=Co, Zn, X=Cl, Br, I; bz=benzimidazole)⁽¹⁴⁻¹⁷⁾. In all cases, the geometry adopted by the metal ion is tetrahedral. The compound dichlorobis (1H-benzimidazole) cobalt(II) reported elsewhere⁽¹⁵⁾ is a type of the above complexes. Coordination compounds containing thiabendazole, 2-(4'-thiazolyl) benzimi-dazole form bis-chelate and tris-chelate compounds⁽¹⁸⁾.

In all cases the ligand coordinates to the metal (cobalt (II), nickel (II), copper (II) zinc(II), cadmium(II) and mercury (II) through the imidazolic and thiazolic nitrogen atoms. In the structure $[Co(btZ-SMe)_2]$, Btz=N-benzo-thiazole-2-yl)

dithiocarbamic methyl ester, the ligand is derivative of benzothiazole, is anionic and behaves as bidentate, nitrogen and sulfur atoms are bonded to the central metal ion giving planar tricyclic chelates, where Co(II) is part of the six-membered ring⁽¹⁹⁾. The symmetrical benzothiazole-based ligand (2,6-bis(benzothiazol-2-yl)-4-(tert-butyl) phenol) and its Cu(II), Ni(II) and Co(II) transition metal complexes were synthesized, the physico-chemical and spectroscopic data show that the complexes may tentatively suggested to octahedral geometry around Ni(II) and Co(II) complexes, and tetragonal geometry for Cu(II) complex, the ligand acts as a bidentate compound coordinating through the nitrogen atom of the benzothiazole group and the oxygen atom of phenol⁽²⁰⁾. In the title complex, $[\text{Cu}(\text{C}_{13}\text{H}_8\text{NOS})_2]$, the Cu(II) atom is coordinated by two N atoms and two O atoms from two bidentate benzothiazolphenolate ligands, forming a distorted tetrahedral geometry [dihedral angle between two N-Cu-O planes: 45.1 (2)]. The dihedral angles between the benzothiazole ring systems and the phenol rings are 4.1 (4) and 5.8 (4), indicating an almost planar geometry. Weak intra and intermolecular C-H...O hydrogen bonds are observed⁽²¹⁾. In view of the reported interesting results and in continuation of our studies on transition metal complexes with sulphur, oxygen and nitrogen containing ligands⁽²²⁻²⁴⁾, This research presents the preparation of new ligands 1,2-(benzothiazole-2-thio)ethane (L^1), 1,2-(benzoxazole-2-thio)ethane (L^2) and 2,6-(benzothiazole-2-thio)pyridine (L^3) (Scheme 1) and their Co(II), Ni(II), Cu(II) and Zn(II) complexes.

MATERIAL AND METHODS

All chemicals were of reagent grade, were used as supplied (Fluka) or (B.D.H). The crystal structure of (L^2) was solved and refined with X-SEED, a graphical interface to SHELX (University of Liverpool, UK)^(25,26). Metal estimation was done on PYE UNICAM SPg atomic absorption spectro-photometer. The chloride was determined using the method in Vogel⁽²⁷⁾.

Conductivity measurements for 10^{-3}M solution of the complexes in (DMF) were carried out by Jenway 4070 conductivity meter. Infrared spectra were recorded on a FTIR Bruker Tensor 27C spectrophotometer in the 200-4000 cm^{-1} range using CsI discs. The UV/Vis spectra were recorded on a Shimadzu UV-160 spectrophotometer for 10^{-3}M solution of complexes in DMF using 1 cm quartz cell. Melting points were measured using an electro thermal 9300 digital melting point apparatus. Magnetic susceptibility was measured on the solid state by Faraday's method using Bruker BM6 instrument at 25°C. All magnetic susceptibility values were corrected for diamagnetic contribution using Pascal's constant. For (L^2) Single crystal X-ray data were collected on a (Bruker D8) diffractometer with an APEX CCD detector, and 1.5 kW graphite monochromated Molybdenum radiations. The structure was solved by direct method and refined by their least squares of F^2 obs by using SHELXL software package⁽²⁸⁾.

General procedure for the synthesis of the ligands (Scheme 1):

1,2-bis-(benzothiazole-2-thio)ethane (L^1): 1,2-dibromoethane (1.88g, 1 mmol) in ethanol (10ml) was boiled under reflux for 6hr. with an equivalent amount of 2-mercaptobenzothiazole (3.34g, 2 mmol) in ethanol (10ml) and NaOH (0.80g, 2 mmol) in ethanol (10ml), after cooling to room temperature, NaBr was removed by filtration. The resulting solution was reduced in volume to ca 1/3, on cooling left a white solid. The solid thus obtained, was filtered off, washed with ethanol and diethylether then dried under vacuum for several hours.

1,2-bis-(benzoxazole-2-thio) ethane (L^2) and 2,6-bis(benzothiazole-2-thio) pyridine (L^3): These ligands were prepared by using similar procedure as above except using 2-mercaptobenzoxazole (3.02g, 2 mmol) in case of (L^2) or (1.48g, 1 mmol) of 2,6-dichloropyridine in case of (L^3).

General procedure for the synthesis metal complexes (Scheme 2): A clear solution of the ligand 1,2-bis (benzothiazole-2-thio)ethane (3.60g, 0.01 mol) in ethanol (10ml) was added to a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or ZnCl_2 (1.0 mmol) in (10ml) ethanol, the reaction mixture was refluxed for 3 hours. Then the mixture was left for 24 hours, at room temperature to give the precipitate which was filtered off, washed with ethanol and diethylether, and then dried under vacuum for 4 hours. A similar procedure was carried out in (L^2) and (L^3) to give their metal complexes.

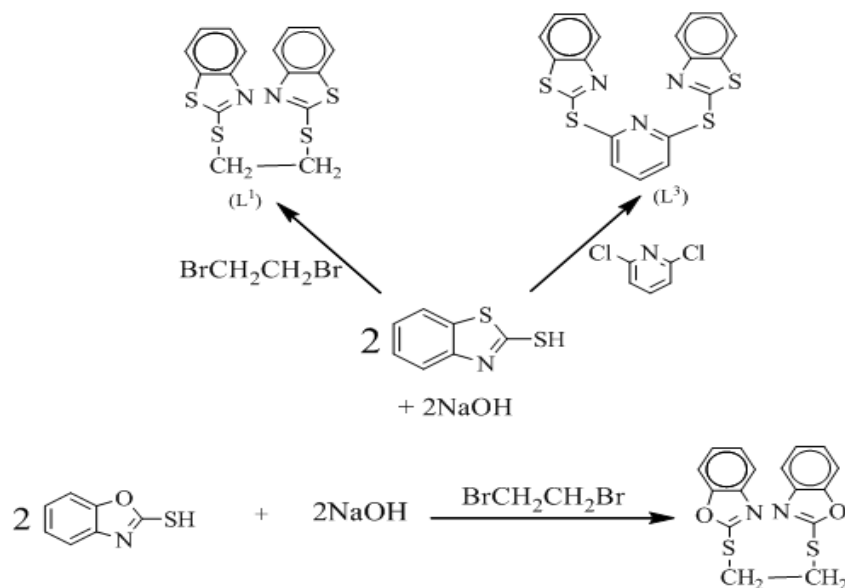


Table 1: Physical properties of ligands

Ligand no.	Chemical formula	Color	m.p. (C ⁰)	Selected IR		Band max. (λ _{max}) nm	Yield %
				v(C=N)	v(-S)		
L ₁	C ₁₆ H ₁₂ N ₂ S ₄	White	142	1600 _s	752 _m	324	85
L ₂	C ₁₆ H ₁₂ N ₂ S ₂ O ₂	Light brown	130	1616 _m	752 _m	296	90
L ₃	C ₁₉ H ₁₁ N ₃ S ₄	White	200 ^d	1614 _m	754 _s	293	92

d=decomposition, S= strong, m=medium

RESULTS AND DISCUSSION

The new tetradentate ligands (L¹),(L³) were prepared by the reaction of 2-mercaptobenzothiazole with 1,2-dibromoethane or 2,6- dichloropyridine to give 1,2- or 2,6-bis (benzothiazole-2-thio) ethane or pyridine while (L²)by the reaction of 2-mercaptobenzoxazole with 1,2-dibromoethane to give 1,2-bis(benzothiazole)ethane in high yield as shown in (Table 1).The complexes were prepared through direct reaction of the metal chlorides, CoCl₂.6H₂O or NiCl₂.6H₂O or CuCl₂.2H₂O or ZnCl₂with the above ligands in (1:1) molar ratio. All the metal complexes except Zn(II) complexes are colored, all of them are stable toward air and moisture. The metal complexes are insoluble in common organic solvents like chloroform, carbon tetrachloride, hexane, methanol and acetone. They are soluble in DMF or DMSO. The analytical data (Table 2) of the metal complexes show that all the metal chelates have 1:1 metal to ligand stoichiometry. Conductance measurements were carried out to ascertain the electrolytic/non electrolytic nature of metal complexes, molar conductance values of complexes in 10⁻³M DMF solution at room temperature suggest the non-electrolytic nature for complexes⁽²⁹⁾ (1-12).

Single crystal X-Ray diffraction

The yellow crystals of (L^2) have been studied by using single crystal X-ray diffraction. The crystal size ($0.200 \times 0.150 \times 0.50 \text{ mm}^3$) and the unit cell dimension $a \neq b \neq c$ ($a=5.8016(3)$, $b=10.1547(5)$, $c=12.3050(6)$ and $\alpha=\gamma \neq \beta$ ($\alpha=90$, $\beta=95.724(2)$, $\gamma=90$) has monoclinic crystal system with $P2_1/n$ space group. (Figure 1) shows drawing of ligand (L^2) and the atom-numbering of this ligand in (Table 3).

Infrared spectral studies: The infrared spectrum of the free ligands shows bands located at $1600-1616$ and $752-754 \text{ cm}^{-1}$ can be assigned to $\nu(C=N)$ and $\nu(C-S)$ respectively. They also showed a band in the region $300-330 \text{ cm}^{-1}$ which may be due to $\nu(M-Cl)$ vibration frequency^(30,31). The $\nu(C-S)$ band in the some complexes was shifted to lower frequency values, while other complexes were shifted upward (Table 4). Further support for this coordination has been provided by the appearance of new bands in the $360-380 \text{ cm}^{-1}$ ranges which are relatively attributed^(32,33) to $\nu(M-S)$.

Magnetic Susceptibility measurements: The magnetic moments are measured at 25°C . The magnetic moments are (4.34-4.67) B.M for Co(II) complexes (1,5 and 9) respectively⁽³⁴⁾, while for Ni(II) complexes (2,6 and 10) are (2.04-3.01), for Cu(II) complexes (3,7 and 11) are (2.04-2.19) B.M. Suggest the presence of one unpaired electron, Zn(II) complexes (4,8,12) are diamagnetic. As the magnetic moment correlate very well with the mononuclear complexes.

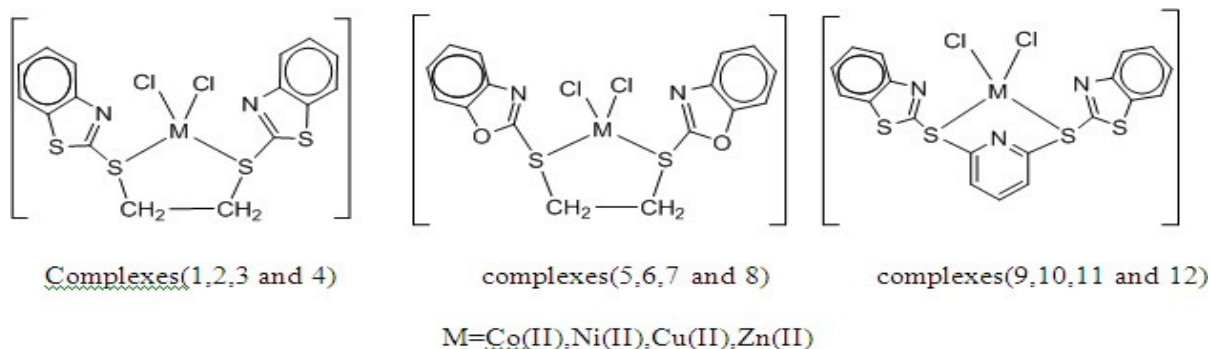
Electronic spectral studies: The UV-Visible spectra of the ligands and their complexes in 10^{-3} M solution DMF were recorded, the results were listed in (Table 3), the bands observed at $293-324 \text{ nm}$ were due to $\pi-\pi^*$ or $n-\pi^*$ transition within the ligands. The spectrum of cobalt (II) complexes (1,5 and 9) show a bands at (608-674)nm. This band is assigned to $^4A_2g \rightarrow ^5E_g(g)$ transition, which is consistent with proposed tetrahedral symmetry of these complexes⁽³⁵⁾. The electronic spectra of Ni(II) complexes (2,6 and 10) showed a band at (692-694) nm were assigned to $^3T_1(F) \rightarrow ^3T_1(P)$ transition in tetrahedral environment around nickel ion^(36,37). The electronic spectra of Cu(II) complexes (3,7 and 11) showed a band at (848-938) nm were assigned to $^2T_2 \rightarrow ^2E$ transition in tetrahedral environment⁽³⁸⁾. The magnetic susceptibility showed that all Zn(II) complexes (4,8 and 12) were diamagnetic and the electronic spectra of these complexes do not show any d-d bands. The ligands used in this study, coordinate to the metal ions in bidentate fashion, from the sulfur atom in the presence of chloride ion in the coordination sphere as shown in (scheme 2).

CONCLUSION

By choosing proper experimental condition, the present investigation was made to synthesized 1,2-bis (benzothiazol-2-thio)ethane, 1,2-bis (benzoxazole-2-thio) ethane, 2,6-bis (benzothiazole-2-thio) pyridine, and their complexes with Co(II), Ni(II), Cu(II) and Zn(II). The above data confirmed 1:1 stoichiometry and the electronic spectral data suggest that the Co(II), Ni(II), Cu(II) and Zn(II) complexes have tetrahedral geometry.

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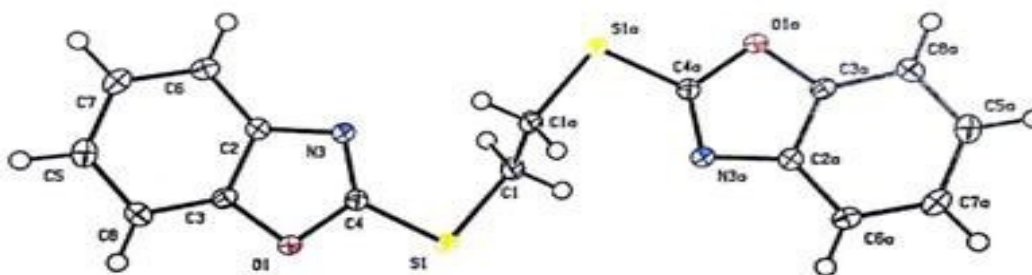


(Scheme2)

Table 2: Physical properties of complexes

complex no.	Structure	Color	m.p	Molar conductivity $\text{Cm}^2.\Omega^{-1}.\text{mol}^{-1}$	μ_{eff}
1	$[\text{Co}(\text{L}_1)\text{Cl}_2]$	Light purple	110-112	25	4.59
2	$[\text{Ni}(\text{L}_1)\text{Cl}_2]$	Light green	178-180	21	2.94
3	$[\text{Cu}(\text{L}_1)\text{Cl}_2]$	Green olive	170 ^d	30	2.18
4	$[\text{Zn}(\text{L}_1)\text{Cl}_2]$	White	120-123	23	Di
5	$[\text{Co}(\text{L}_2)\text{Cl}_2]$	Purple	158-160	36	4.67
6	$[\text{Ni}(\text{L}_2)\text{Cl}_2]$	Green yellowish	150-152	29	3.01
7	$[\text{Cu}(\text{L}_2)\text{Cl}_2]$	Darkbrown	110-112	24	2.04
8	$[\text{Zn}(\text{L}_2)\text{Cl}_2]$	White	244-246	33	Di
9	$[\text{Co}(\text{L}_3)\text{Cl}_2]$	Dark blue	144 ^d	36	4.34
10	$[\text{Ni}(\text{L}_3)\text{Cl}_2]$	Brown	148 ^d	21	2.88
11	$[\text{Cu}(\text{L}_3)\text{Cl}_2]$	Dark brown	188-190	25	2.19
12	$[\text{Zn}(\text{L}_3)\text{Cl}_2]$	White	180-182	26	Di

d=decomposition

**Figure-1: L2=1,2-bis-(benzoxazole-2-thio)ethane****Table 3: Crystal data and structure refinement for L²=1,2-bis-(benzoxazole-2-thio)ethane**

Empirical formula	$\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}_2\text{O}_2$
Formula weight	328.40
Temperature/K	99.99
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions:	
a/Å	5.8016(3)

b/Å	10.1547(5)
c/Å	12.3050(6)
$\alpha/^\circ$	90.00
$\beta/^\circ$	95.724(2)
$\gamma/^\circ$	90.00
Volume/ Å ³	721.32(6)
Z	2
$P_{\text{calc}}/\text{mg}/\text{mm}^3$	1.512
m/mm^{-1}	0.377
F(000)	340.0
Crystal size/ mm^3	0.200 x 0.150 x 0.050
Theta range for data collection	5.22 to 52.84 $^\circ$
Index ranges	-7<=h<=7, -12<=k<=12, -15<=l<=15
Reflections collected	9156
Independent reflections	1482 [R(int) = 0.0213]
Data / restraints / parameters	1482/0/124
Goodness-of-fit on F ²	1.085
Final R indices [I>2 σ (I)]	R1 = 0.0255, wR2 = 0.0698
R indices (all data)	R1 = 0.0261, wR2 = 0.0706
Largest diff. peak and hole/ e.Å ⁻³	0.24 and -0.27

Table 4: Electronic and infrared spectral data of complexes

complex no.	nd maxima (λ_{max}) nm	$\nu(\text{=N})$	$\nu(\text{C-S})$	$\nu(\text{M-S})$	$\nu(\text{M-Cl})$	
1	314,608		1603 _m	744 _s	377 _m	327 _w
2	306,692		1601 _w	731 _m	375 _m	315 _w
3	304,938		1600 _s	735 _m	370 _m	321 _m
4	306		1600 _m	743 _s	368 _w	300 _w
5	292,610		1618 _s	739 _s	370 _m	322 _w
6	300,696		1614 _m	746 _s	360 _s	312 _m
7	311,938		1614 _w	742 _m	380 _m	317 _w
8	288		1616 _w	739 _s	366 _m	323 _s
9	313,674		1616 _w	743 _w	370 _m	322 _m
10	316,694		1616 _m	775 _m	375 _m	325 _m
11	318,848		1614 _m	744 _m	380 _m	315 _w
12	326		1612 _w	768 _m	372 _m	310 _s

S= strong, m=medium, w= weak

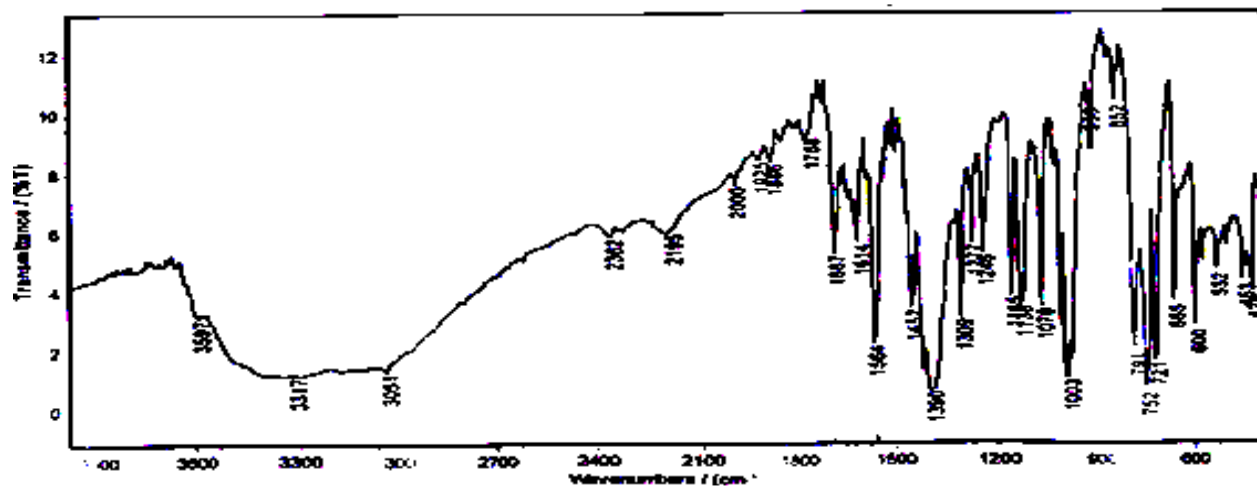


Figure 2: Infrared spectra of (L^3)

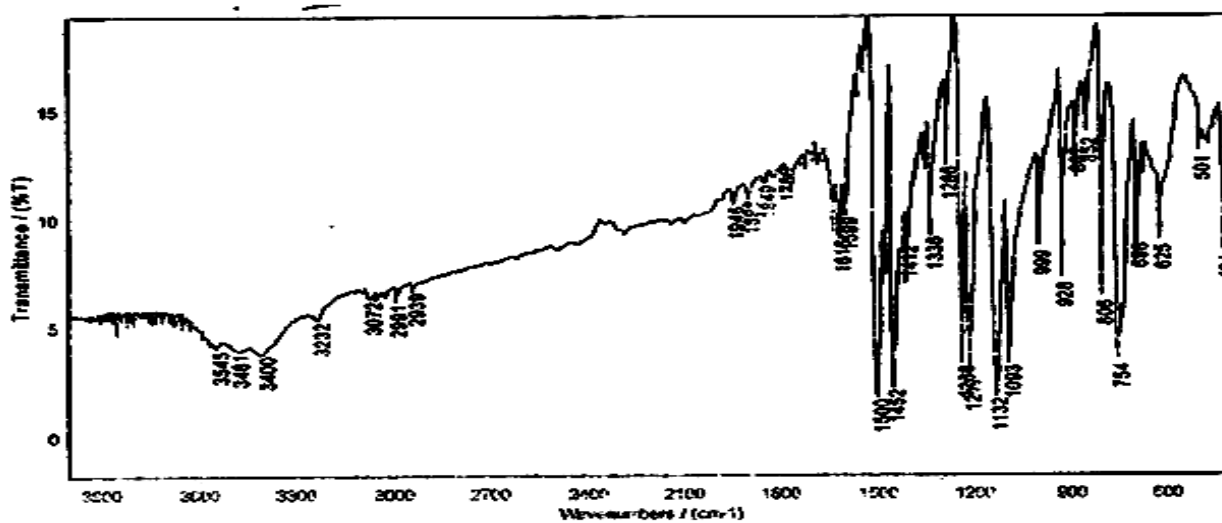


Figure 3: Infrared spectra of (L^2)

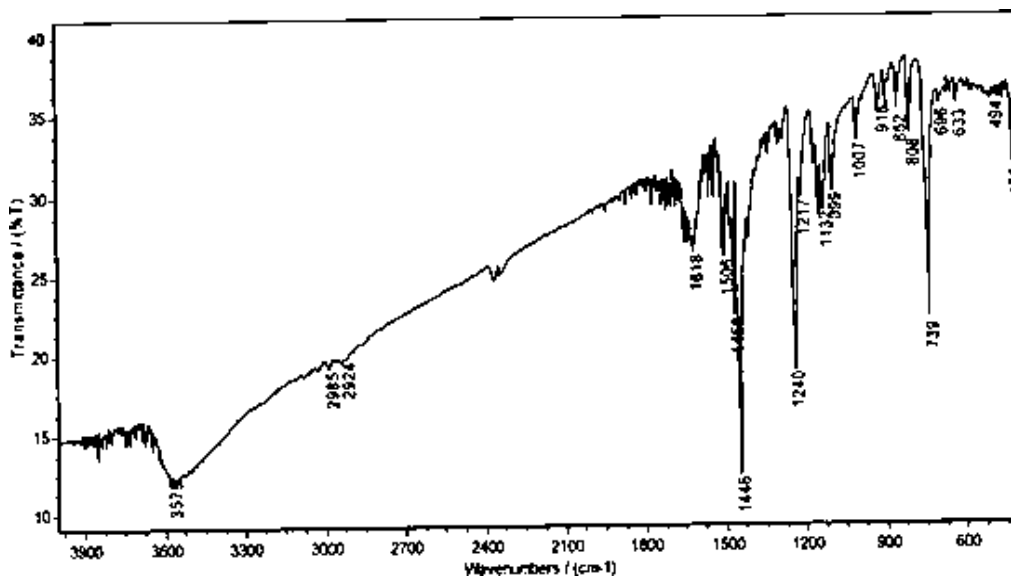


Figure 4: Infrared spectra of $[Zn(L^2)Cl_2]$

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