



Synthesis and Structural Studies on Some Transition metal complexes of Bis-(benzimidazole-2-thio) ethane, propane and butane 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-(benzimidazole-2-thio) ethane, $L^2 = 1,3$ -bis-(benzimidazole-2-thio) propane, $L^3 = 1,4$ -bis-(benzimidazole-2-thio)butane], derived from the condensation of 2-mercaptobenzimidazole and 1,2-dibromoethane or 1,3-dibromo propane or 1,4-dibromobutane were synthesized. Characterization has been done on the basis of analytical conductance, magnetic data, infrared, electronic spectra, metal content analysis and $^1\text{H NMR}$ data for the ligands. 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 N,N or S,S or S,S,N,N donor sequence toward the metal ions. On the basis of the above spectral, physicochemical, data as well as magnetic moment measurements tetrahedral and square planar geometries were assigned for the complexes.

Keywords: Metal complexes, benzimidazole-2-thio derivatives, spectral study.

Introduction

Interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor groups¹⁻² and it is multiplied many fold when the ligand have biological importance³⁻⁴. Benzimidazoles are involved in a great variety of biological processes. Some of their poly functional derivatives have been proven to possess antibacterial, fungicide and anti-hermitic activity⁵⁻⁸. Therefore substituted benzimidazoles 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 effect⁹. Several groups have reported cobalt (II) and Zn(II) coordination compounds showing a similar stoichiometry $[\text{M}(\text{bz})_2\text{X}_2]$ ($\text{M}^{\text{II}} = \text{Co}, \text{Zn}, \text{X} = \text{Cl}, \text{Br}, \text{I}; \text{bz} = \text{benzimidazole}$)¹⁰⁻¹³. In all cases, the geometry adopted by the metal ion is tetrahedral. The compound dichloro bis (1H-benzimidazole)-cobalt(II) reported elsewhere¹⁰ is a type of the above complexes. Coordination compounds containing thiabendazole, 2-(4'-thiazolyl) benzimidazole form bis-chelate and tris-chelate compounds¹⁴. 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. The spiracyclic structure $[\text{Co}(\text{btz-SMe})_2]$, 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 rings¹⁵. The crystal structures of Co(II) and Ni(II) complexes of 4-(benzimidazole-2-yl)-3-thiabutanoic acid which provide a benzimidazole, a thioether and carboxyl donor group. The crystal structure of Cu(II) complex indicates that the two oxygen and two nitrogen donors for a square coordination

around the copper ion, while the two sulfur are approximately axial to the copper center¹⁶. In view of the reported interesting results and in continuation of our studies on transition metal complexes with sulphur, oxygen and nitrogen containing ligands¹⁷⁻¹⁹, we are presenting here the preparation of new ligands 1,2 or 1,3 and 1,4-(benzimidazole-2-thio) ethane (L^1), propane (L^2) and butane (L^3) Scheme-1 and their Co(II), Ni(II), Cu(II) and Zn(II) complexes.

Material and Methods

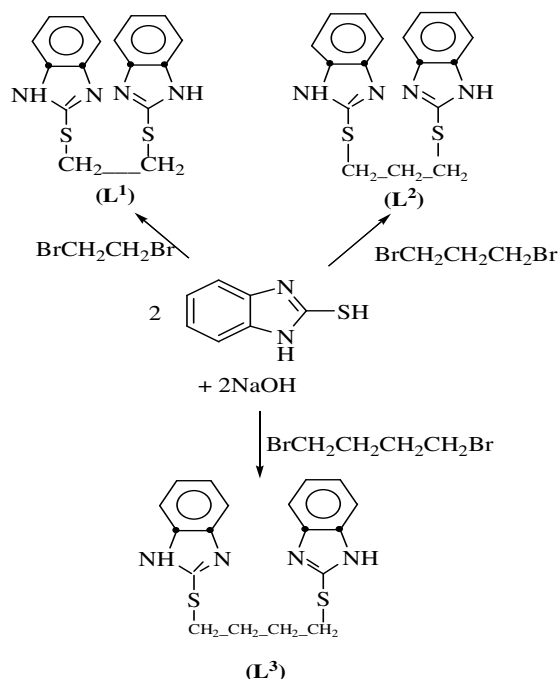
All chemical were of reagent grade, were used as supplied (Fluka) or (B.D.H). Elemental analyses (C,H,N and S) were carried out using micro analytical techniques on Perkin Elmer 2400 (IEES) at AL-AL-bayt University (Jordan). Metal estimation were done on PYE UNICAM SPg atomic absorption spectro-photometer. The chloride was determined using the method in Vogel²⁰. Conductivity measurements for 10^{-3}M solution of the complexes in (DMF) were carried out with on Jenway 4070 conductivity meter and a dip cell with platinized electrode. Infrared spectra were recorded on a FTIR Bruker Tensor 27co 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 point were measured using an electrothermal 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 susceptibilities values were corrected for diamagnetic contribution using Pascal's constant. $^1\text{H NMR}$ spectra of the ligands were carried on varian 300 MHz NMR spectrometer. Chemical shifts are reported in ppm relative to an internal standard of TMS.

General procedure for the synthesis of the ligands (Scheme-1): **1, 2-bis-(benzimidazole-2-thio)ethane (L¹):** 1,2-dibromoethane (1.88g,1mmol) in ethanol (10ml) was boiled under reflux for 6hr. with an equivalent amount of 2-mercapto-benzimidazole (3.00g,2mmol) and NaOH (0.80g,2mmol) in ethanol (20 ml) , 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.

1,3-bis-(benzimidazole-2-thio)propane (L²) and 1,4-bis(benzimidazole-2-thio) butane (L³) : These ligands were

papered by using similar procedure as above except using 1,3-dibromopropane (2.02g,0.01mol) in case of (L²) or (2.16g,0.01 mol) of 1,4-dibromobutane in case of (L³).

General procedure for the synthesis metal complexes (Scheme-2): A clear solution of the ligand 1,2-bis (benzimidazole-2-thio)ethane (3.26g , 0.01 mol) in ethanol (20ml) was added to a solution of CoCl₂.6H₂O or NiCl₂.6H₂O or CuCl₂.2H₂O or ZnCl₂ (1.0 mmol) in (10ml) ethanol, the reaction mixture was refluxed for 2 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, then dried under vacuum for 4 hours.



Scheme -1

Table-1
Physical properties of ligands

Ligand no.	Chemical formula	Color	m.p.	Analysis found (calc.) %				Selected IR		Band max. (λ _{max}) nm	Yield %
				C	H	N	S	ν (C=N)	ν (C-S)		
L ₁	C ₁₆ H ₁₄ N ₄ S ₂	white	256	58.57 (58.87)	5.27 (4.28)	17.59 (17.15)	20.07 (19.54)	1589 _s , 1637 _s	744 _s	312	92
L ₂	C ₁₇ H ₁₆ N ₄ S ₂	white	231	59.98 (59.97)	5.53 (4.69)	16.54 (16.44)	19.30 (18.83)	1655 _s	742 _s	314	89
L ₃	C ₈ H ₁₈ N ₄ S ₂	white	275 ^d	61.11 (60.94)	5.98 (5.07)	15.32 (15.79)	18.48 (18.09)	1588 _m	746 _s	306	93

d=decomposition, S= strong, m=medium

Results and Discussion

The new tetradentate ligands (L^1), (L^2) and (L^3) were prepared by the reaction of 2-mercaptobenzimidazole with 1,2-dibromoethane or 1,3-dibromopropane or 1,4-dibromobutane to give 1,2 or 1,3 or 1,4-bis (benzimidazole-2-thio) ethane or propane or butane in high yield table 1. The complexes were prepared through direct reaction of the metal chlorides, $CoCl_2 \cdot 6H_2O$ or $NiCl_2 \cdot 6H_2O$ or $CuCl_2 \cdot 2H_2O$ or $ZnCl_2$ with 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, 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 $10^{-3}M$ DMF solution at room temperature suggest the non electrolytic nature for complexes (1-8) and (1:2) electrolytic nature for the complexes (9-12) ²¹.

¹HNMR data: The ¹HNMR spectrum of the ligands (L^1), (L^2) and (L^3) were recorded in DMF-d7 solution. The results showed that the position of δ 11.83-12.47 NH protons (S,2H of benzimidazole), a multiple at δ 6.95- δ 7.25 due to aromatic protons and δ 1.63-3.75 for alkyl protons. For (L^1) δ 12.47 NH protons (S,2H, of benzimidazole), a multiplet at δ 7.09 – δ 7.52 (8H) due to aromatic protons, δ 3.75 (d,4H,S-CH₂), where as for (L^2) δ 12.47 NH protons (S,2H of benzimidazole) , a multiplet at δ 7.11- δ 7.44 (8H) is due to aromatic protons, δ 1.90 (S,2H,CH₂) and δ 2.19,4H,SCH₂) while for L^3 δ 11.86 NH protons (S,2H, of benzimidazole), a multiple at δ 7.11- δ 7.58 (8H) is due to aromatic protons, δ 1.63 (m, 4H and δ 2.11, 4H,SCH₂). The ¹HNMR signals are in correlation with the expected structure scheme-1

Infrared spectral studies: The infrared spectrum of the free ligands shows strong band in the region 3330-3390 cm^{-1} which is assignable NH of benzimidazole ring. Strong bands located at 1578-1589, 1637-1655 and 742-746 cm^{-1} can be assigned to $\nu(C=N)$ and $\nu(C-S)$ respectively. A negative and positive shift in $\nu(C=N)$ to extent of (11-23) or (10-18) cm^{-1} in the spectra of the chelates suggest the involvement of azomethine nitrogen benzimidazole ring in coordination ²² (figure 1, 2 and 3). Further support for this argument came from the IR of the complexes which showed new a bands at 480-499 cm^{-1} attributed to $\nu(M-N)$. They also showed a band in the region 300-330 cm^{-1} which may be due to $\nu(M-Cl)$ vibration frequency ^{23,24}. The $\nu(C-S)$ band in the some complexes was shifted to lower frequency values, while other complexes was shifted upward table-3. Further support for this coordination has been provided by the

appearance of new bands in the 360- 380 cm^{-1} ranges which are relatively attributed to $\nu(M-S)$ ^{25,26}.

Magnetic Susceptibility measurements: The magnetic moments are measured at 25°C. The magnetic moments are (4.38-5.08) B.M for Co(II) complexes (1,5 and 9) respectively, while for Ni(II) complexes (2,6 and 10) are diamagnetic , for Cu(II) complexes (3,7 and 11) are (1.53-2.23) 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.

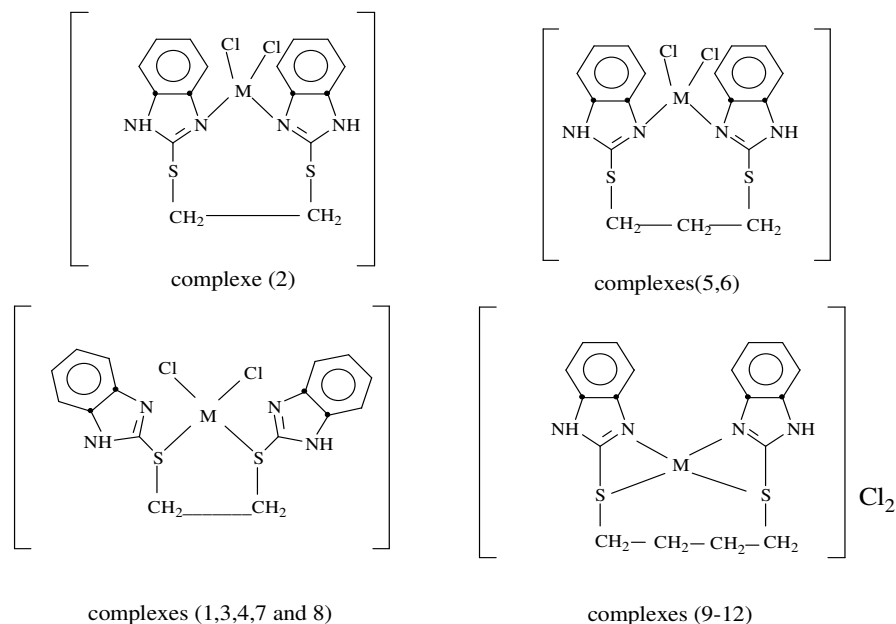
Electronic spectral studies: The UV-Visible spectra of the ligands and their complexes in $10^{-3} M$ solution DMF were recorded, the results were listed in Table-3, the bands observed at 306-314 nm were due to $\pi-\pi^*$ or $n-\pi^*$ transition within the ligands. The spectrum of cobalt (II) complexes (1,5 and 9) show a bands at (610-690)nm. This band is assigned to $^4A_2g \rightarrow ^4T_1g$ (p) transition, which is consistent with proposed tetrahedral symmetry of these complexes. Further the blue colors of these complexes support its proposed tetrahedral geometry ²⁷. The diamagnetic nature of nickel (II) complexes (2,6 and 8) and the appearance of the bands at (574-678) and (408-430) nm were assigned to $^1A_1g \rightarrow ^1A_2g$ and $^1A_1g \rightarrow ^1B_1g$ transition in a square planer environment around nickel ion ^{17,28}. The electronic spectra of Cu(II) complexes (3,7 and 11) showed a band at (810-848) nm were assigned to $^2T_2 \rightarrow ^2E$ transition in tetrahedral environment ²⁹. 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 band. The ligands used in this study, coordinate to the metal ions in bidentate or tetrah-edentate fashion, from the azom-ethine nitrogen benzimidazole ring or sulfur atoms or both azomethine nitrogen benzimidazole ring and sulfur atoms in the presence of chloride ion in the coord-ination sphere or outside the coordination sphere as shown in scheme-2.

Conclusion

By choosing proper experimental condition, the present investigation was made to synthesized 1,2;1,3 and 1,4-bis (benzimidazole-2-thio)ethane or propane or butane and their complexes with Co(II),Ni(II),Cu(II) and Zn(II). From the result , discussion and analysis data it is conformed 1:1 stoichiometry and the electronic spectral data suggest that the Ni(II) complexes have square planer geometry where as Co(II) ,Cu(II) and Zn(II) complexes have tetrahedral geometry.

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(Schem-2)

Table-2

Physical properties of complexes

complex no.	structure	color	m.p	Analysis found (calc.) %						Molar conductivity $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	μ_{eff}
				C	H	N	S	M	Cl		
1	$[\text{Co}(\text{L}_1)\text{Cl}]_2$	Blue	210 ^d	43.77 (42.08)	3.08 (3.06)	13.17 (12.27)	14.90 (14.05)	12.59 (12.91)	15.08 (15.54)	21	4.38
2	$[\text{Ni}(\text{L}_1)\text{Cl}]_2$	Light brown	209 ^d	42.45 (41.85)	3.67 (3.07)	13.21 (12.28)	14.98 (14.06)	11.42 (12.87)	15.11 (15.54)	34	Di
3	$[\text{Cu}(\text{L}_1)\text{Cl}]_2$	Light brown	159 ^d	42.02 (41.66)	3.67 (3.03)	13.09 (12.15)	14.84 (13.91)	13.44 (13.78)	14.59 (15.38)	23	2.22
4	$[\text{Zn}(\text{L}_1)\text{Cl}]_2$	White	252-254	42.00 (41.49)	3.54 (3.02)	13.43 (12.10)	14.31 (13.85)	13.77 (14.13)	14.15 (15.32)	30	Di
5	$[\text{Co}(\text{L}_2)\text{Cl}]_2$	Blue	173 ^d	44.24 (43.37)	3.99 (3.40)	12.83 (11.90)	14.34 (13.63)	11.63 (12.53)	14.90 (15.07)	39	4.79
6	$[\text{Ni}(\text{L}_2)\text{Cl}]_2$	Brown	212 ^d	44.12 (43.40)	3.87 (3.40)	12.01 (11.91)	14.65 (13.64)	11.31 (12.48)	14.97 (15.08)	35	Di
7	$[\text{Cu}(\text{L}_2)\text{Cl}]_2$	Light yellow	250 ^d	43.55 (42.95)	4.10 (3.36)	12.46 (11.79)	14.04 (13.50)	12.88 (13.38)	14.10 (14.93)	26	1.53
8	$[\text{Zn}(\text{L}_2)\text{Cl}]_2$	White	248-250	44.13 (43.33)	3.71 (3.39)	12.41 (11.89)	14.70 (13.62)	12.96 (13.71)	14.58 (14.87)	37	Di
9	$[\text{Co}(\text{L}_3)\text{Cl}]_2$	Dark blue	273 ^d	44.98 (44.60)	3.89 (3.71)	12.11 (11.56)	14.12 (13.24)	11.25 (12.16)	14.40 (14.64)	150	5.08
10	$[\text{Ni}(\text{L}_3)\text{Cl}]_2$	Light brown	218 ^d	44.71 (44.62)	3.91 (3.71)	12.09 (11.56)	14.43 (13.24)	11.37 (12.12)	14.62 (14.64)	129	Di
11	$[\text{Cu}(\text{L}_3)\text{Cl}]_2$	Rusty	143 ^d	44.98 (44.18)	3.89 (3.68)	12.23 (11.45)	14.55 (13.11)	12.58 (12.99)	14.86 (14.50)	163	2.07
12	$[\text{Zn}(\text{L}_3)\text{Cl}]$	White	210-212	44.70 (44.01)	3.88 (3.66)	12.09 (11.41)	14.12 (13.06)	12.82 (13.32)	14.77 (14.44)	133	Di

d=decomposition

Table-3
 electronic and infrared spectral data of complexes

complex no.	Band maxima (λ_{max}) nm	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{S})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{Cl})$
1	314,610,666	1637 _s ,1589 _m	762 _s	----	360 _m	310 _w
2	318,624,664	1651 _s ,1577 _m	744 _m	482 _m	---	325 _w
3	320,472,636	1637 _s	731 _m	---	380 _m	312 _w
4	332,684	1637 _s	755 _s	---	370 _m	320 _w
5	322,610,670	1637 _s	746 _s	480 _m	---	300 _w
6	306,624,692	1637 _s	744 _s	492 _m	---	330 _w
7	318,340	1655 _s	735 _s	---	360 _w	325 _w
8	322,574,608	1655 _s	758 _m	---	380 _m	315 _w
9	308,610,668	1577 _m	762 _s	488 _m	370 _m	---
10	302,618,692	1570 _s	756 _s	492 _s	375 _m	---
11	334,434	1565 _s	732 _s	484 _m	380 _w	---
12	302,572,600	1572 _s	732 _s	499 _m	370 _m	---

S= strong, m=medium, w= weak

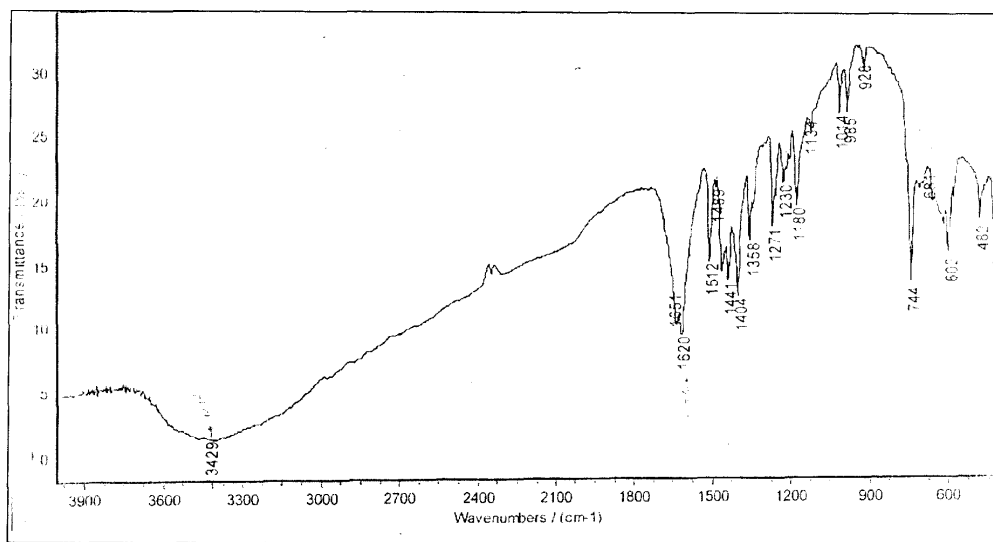


Figure-1

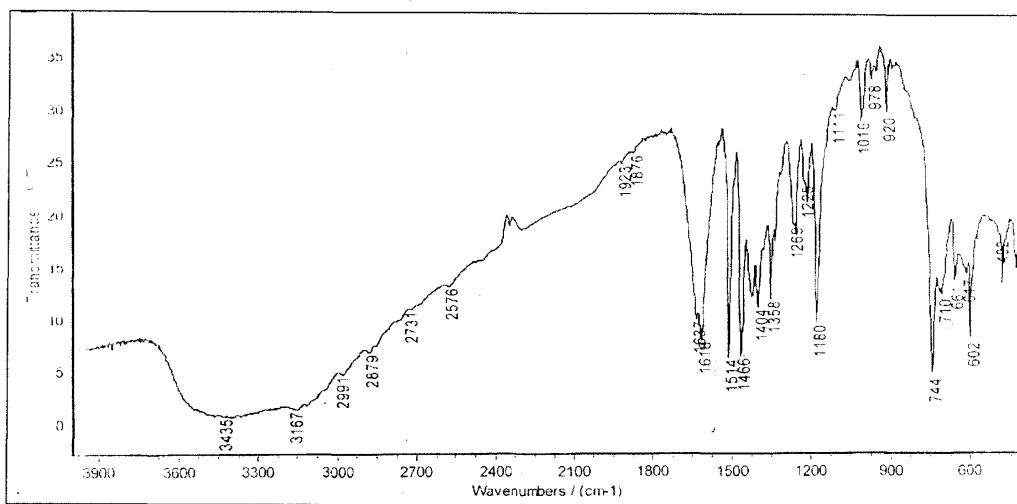


Figure-2

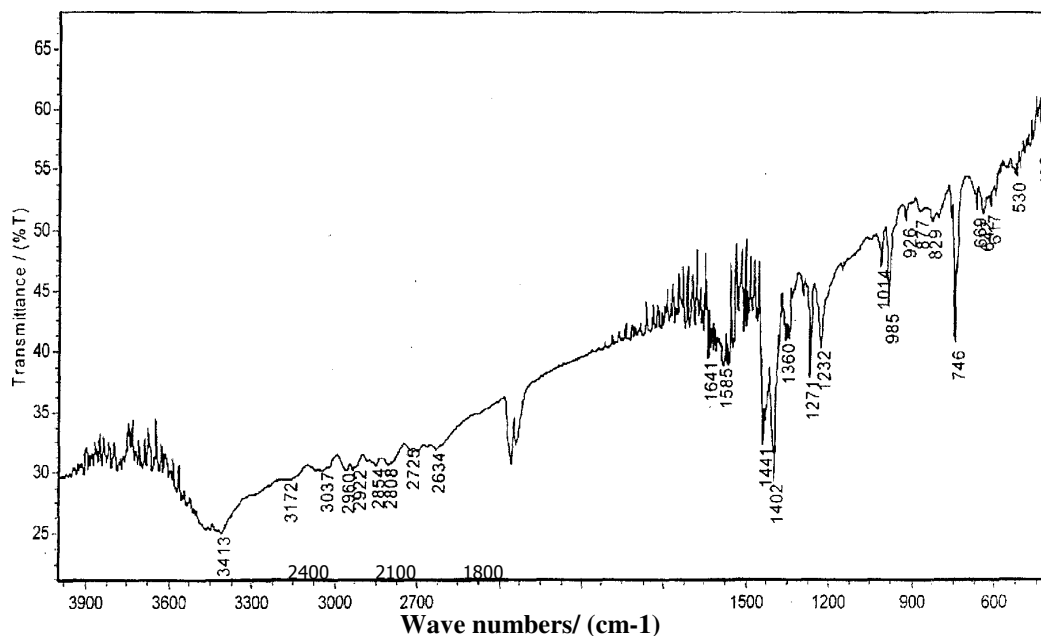


Figure-3
Infrared spectra of $[\text{Co}(\text{L}^3)]\text{Cl}_2$

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