Synthesis, Characterization And Biological Studies Of Some Bimetallic Bridged Thiocyanate Schiff Base Complexes Based On Carbohydrazide

Asraa Tuaama Kasid[1*], **Mouayed Yousif Kadhum**[2]

[1*]Department of Chemistry, College of Education for pure science, University of Basrah, Basrah, Iraq
[2]Department of Chemistry, College of Education for pure science, University of Basrah, Basrah, Iraq

***Corresponding Author: -** Asraa Tuaama Kasid

*Department of Chemistry, College of Education for pure science, University of Basrah, Basrah, Iraq
Doi: 10.47750/pnr.2022.13.S05.291

Abstract

Two new Schiff base ligands (L_1,L_2) were prepared from reaction of carbohydrazide with 3,4-dihdroxybenzaldehyde or morpholinecarboxaldehyde. These ligands were reacted with MM`(SCN)$_4$ [M=$Co^{+2}$, $N^{+2}$, M`=Cd^{+2}] to produced four new complexes. These compounds were characterized by elemental analysis, infrared, ultraviolet-visible, ^{1}H, ^{13}C-NMIR, mass spectra, molar conductivity, and magnetic susceptibility. The prepared Schiff bases are regarded as bidentate ligands. All complexes are non-electrolytes and have coordination number equal four. The ligands and their complexes are screened for antibacterial and antifungal activity against some microorganisms and found that these compounds have a good antimicrobial activity.

Keywords: Schiff base, binuclear complexes, thiocyanate , Synthesis, biological activity

INTRODUCTION

Under particular circumstances, condensation reactions between primary amines and aldehydes or ketones produce Schiff bases. Schiff bases play a significant role in a variety of catalytic and industrial processes, diverse biological functions, and the capacity to stabilize metal ions in various oxidation states (1,2). A unique class of ligands known as schiff bases include a range of donor atoms that exhibit intriguing coordination patterns toward different metals. Schiff bases' biological actions, including their anticancer, antibacterial, antifungal, and herbicidal effects, are caused via the azomethine linkage (3). Numerous Schiff base complexes exhibit strong catalytic activity in a variety of processes, and both homogeneous and heterogeneous catalysis have seen extensive use of these compounds. moreover, Schiff base complexes are made for their fascinating and significant qualities, including their capacity to reversibly bind oxygen, their propensity to combine with several hazardous metals, and the advancement of contemporary coordination chemistry and optical materials (4-6). Because these substances include SCN bridges, which link metal atoms to build limitless two-dimensional or three-dimensional networks, tetrathiocyanate complexes with Schiff base ligands are the subject of intense research (7,8).

In the present paper we report the synthesis, physical spectral Properties and biological activity of new bidentate Schiff ligands and their binuclear thiocyanate complexes with general formula MM` (SCN)$_4$.L where M = Co (II) or Ni (II) , L = Schiff base ligand .

MATERIALS

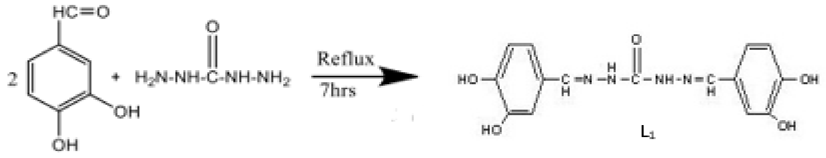
All chemicals, analytical reagents and metal salts were purchased and received without further purification. Carbohydrazide, 3,4-dihdroxybenzaldehyde and morpholine carboxaldehyde from Fluka company. Potassium thiocyanate, DMSO, methanol, (cobalt (II), nickel (II) nitrate) and ethanol from Sigma company.

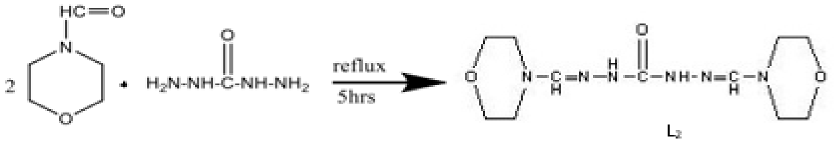
INSTRUMENTS

Elemental analysis of the prepared compounds was recorded on ECS-4010 CHNSO analyzer. Infrared spectra were recorded in the range 400-4000 cm^{-1} by KBr Pellet using FT-IR 84005 Shimadzu spectrophotometer at the room temperature. Melting points of the ligands and complexes were determined in electro-thermal fisher apparatus. ^{1}HNMR and ^{13}CNMR spectra in DMSO-d$_6$ were recorded on NMR spectrophotometer (Varian-500 MHZ). Electronic spectra of the compounds were obtained in ethanol on UV 1800 Shimadzu. The metal content of the complexes were determined by atomic absorption on phoenix-986 AA spectrophotometer. The magnetic susceptibility of the complexes was recorded on MSB-MKI at room temperature by Faraday method. Conductance was measured in DMF at room temperature using Jenway pcmb conductivity meter. Mass spectra of the ligands were recorded by MS model:5975C VL MSD (EI)70 ev.

Synthesis of Schiff base ligands

Ligand L_1 was synthesized according to a literature procedure (9) (0.004mol) 0.55g of 3,4- dihydroxybenzaldehyde was dissolved in 25 ml ethanol . (0002mol) 0.18g of carbohydrazide was dissolved in 25 ml ethanol. The two solutions were mixed and catalyzed by amount of glacial acetic acid. The reaction mixture was subjected to reflux conditions for 7 hours. The product was collected by filtration and washed with hot ethanol (melting point of 235 ºC, yield of 82 %) . The second ligand L_2 was synthesized in the same way using morpholinecarboxaldehyde and carbohydrazide (melting point of 155 ºC, yield of 86%) as shown in equations :

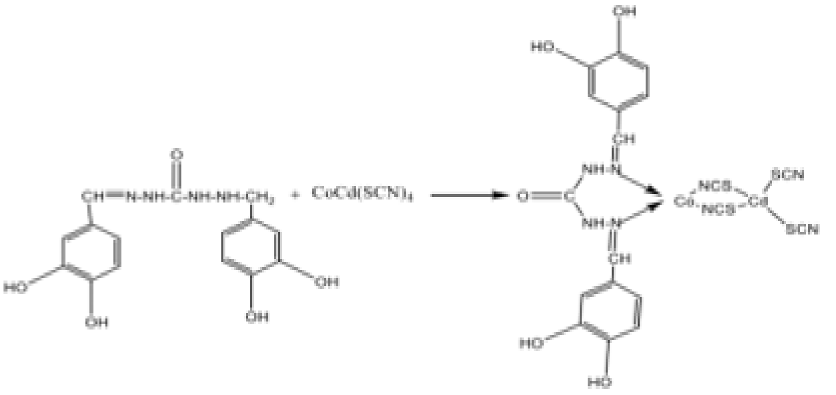




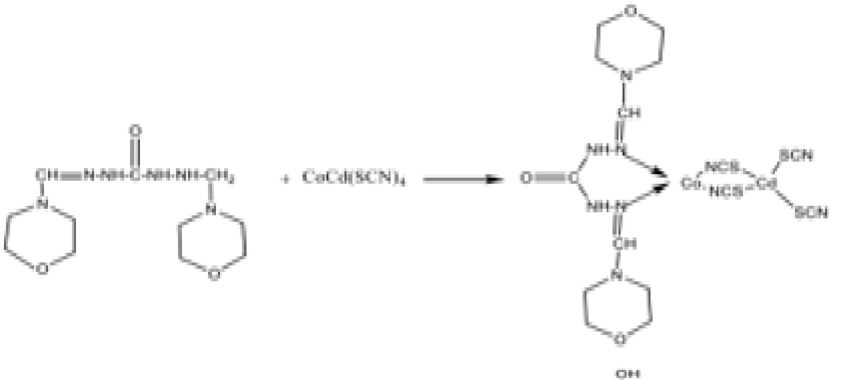
Synthesis of thiocynate complexes

Metal dithiocyanate [$Co(SCN)_2$, $Ni(SCN)_2$, $Cd(SCN)_2$] were Synthesized as a Similar paper (10) by the reaction of metal nitrate with potassium thiocyanate in methanol. The formed potassium nitrate was removed by filtration . The solutions of dithiocyanates were kept for further reaction.

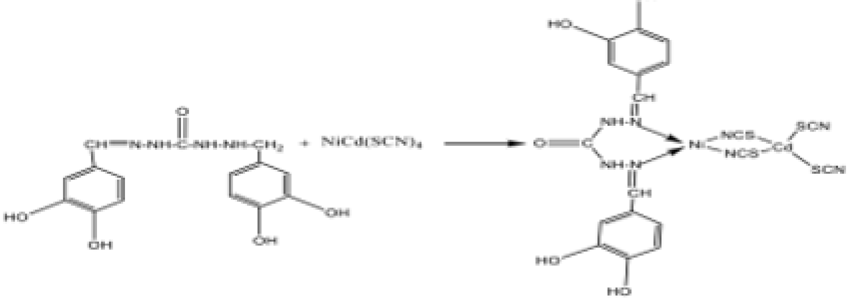
Tetrathiocyanates MM\` $(SCN)_2$ [M= Co, Ni, M\`=Cd] were synthesized by mixing solution of $M(SCN)_2$ and $M^{-}(SCN)_2$ in 1:1 molar ratio and stirred for 36 hrs. Solution of these tetra thiocyanates as alone in methanol was mixed with synthesized ligands L_1 or L_2 in same solvent in 1:1 molar ratio. Solid product was formed, filtered and washed with ether (L_1Co, m.p 270 ºC, yield 76%) (L_2Co, m.p 213 ºC , yield 78%) (L_1Ni ,m.p 280 ºC , yield 90%) (L_2Ni ,m.p 204 ºC , yield 80%) as shown in equations : .



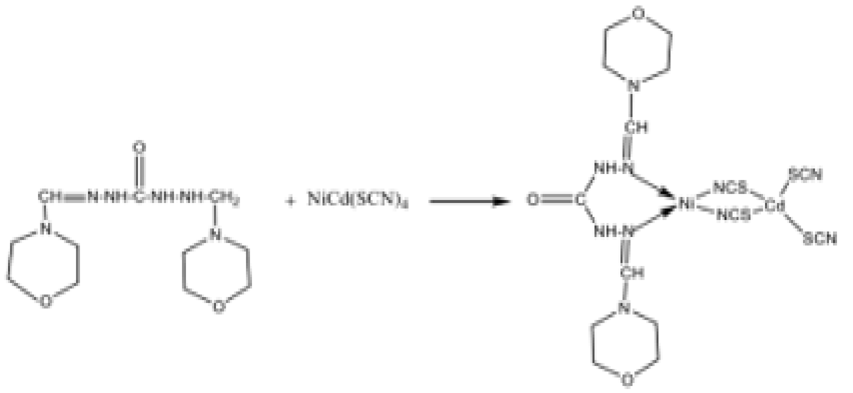
L_1Co



L_2Co



L_1Ni



L2Ni

RESULTS AND DISCUSSION

The results of elemental analysis for prepared ligands and their complexes show that the percentages of carbon, hydrogen, nitrogen, cobalt and nickel are equivalent to calculated values as shown in table (1). This is evidence that proposed chemical structures of these compounds are true .

The important infrared spectral bands of the prepared ligands and complexes are presented in figures (1-6) and table (2). In the ligands L_1,L_2 the characteristic absorption frequencies belonged to azomethine group were appeared at 1620 cm^{-1} and 1641 cm^{-1} respectively, while in their complexes were shifted to lower frequencies, indicating the participation of the azomethine nitrogen in interaction with the metal ion (11) . The infrared spectra of prepared complexes show new bands at (2073-2080) cm^{-1} which are assigned to C-N in nitrogen bonded thiocyanate (M-NCS) and (2135-2150) cm^{-1} in sulfur bonded thiocyanate (M-SCN) (12). Also it is observed that bands at (745-750) cm^{-1} belong to the stretching vibration of S-C in the bridged thiocyanate (13) . Also the complexes show new bands at (522-535) cm^{-1} due to the formation of M-N bonds(14) .

UV-visible spectra of the Schiff base ligands (L_1,L_2) shown in figures (7,8) were appeared absorption bands at 290 nm and 302nm respectively due to π-π^*transition for azomethine moiety. The transitions at 314nm(L_1) and 359nm(L_2) were assigned to π- π^* belonged to double bonds in aromatic cycles and carbonyl group respectively . In the spectra of complexes shown in figures (9-12), the absorption bands belonged to azomethine group are shifted to lower or higher wavelengths compared to ligands indicating that the imine nitrogen is involved in the coordination with metal ion(15,16) . Also it is observed, absorptions in the ultraviolet region were weak due to d-d transition (17).

^{1}HNMR and ^{13}CNMR spectra of the ligands shown in figures (13-16) were appeared the expected signals as a signed in table (3) .

The mass spectra of the ligands (L_1,L_2) shown in figures (15,16) were indicated appearance of molecular ion at m/z=230.1($C_{15}H_{14}N_4O_5^{\cdot+}$) and m/z=284.3($C_{11}H_{20}N_6O_3^{\cdot+}$) respectively . Also, important peaks (base ions) were appeared in L_1 at m/z=151.1 ($C_7H_7N_2O_2^{\cdot+}$) and in L_2 at m/z=42.1 ($CH_2N_2^{\cdot+}$) . Moreover, the mass spectra of the ligands were assigned another peaks corresponding to their various fragments.

Molar conductivity data were listed in table (4) indicating that all the complexes were non electrolytic. The magnetic moment μ_{eff} values shown in table (4) were indicated that the complexes (L_1Co , L_2Co) have tetrahedral geometry and paramagnetic properties while the complexes (L_1Ni , L_2Ni) were square planer and diamagnetic properties.

The antibacterial and antifungal activities of Schiff base ligands and their complexes were studied against (Staphylococcus, E.coli (bacteria)) and (Candida , Aspergillus (Fungi)) as shown in table (5). The results indicated that all compounds have good activity due to the presence of azomethine group and some important functional groups.

Table 1: Elemental analysis data of the ligands and their complexes

Symb.of Compound	Formula M.wt (g/mol)	C%		H%		N%		Co%		Ni%	
		found	cal.	found	cal.	found	cal.	found	cal.	Found	cal.
L_1	$C_{15}H_{14}N_4O_5$ 330.32	54.37	54.55	4.21	4.27	16.87	16.96	-	-	-	-
L_2	$C_{11}H_{20}N_6O_3$ 284.34	46.35	46.47	6.98	7.09	29.43	29.56	-	-	-	-
L_1Co	CoCd $(SCN)_4C_{15}H_{14}N_4O_5$ 748.99	32.51	32.07	2.25	2.29	14.93	14.96	7.13	7.87	-	-
L_1Ni	$NiCd(SCN)_4C_{15}H_{14}N_4O_5$ 748.75	32.35	32.08	2.37	2.29	15.11	14.97	-	-	7.13	7.84
L_2Co	$CoCd(SCN)_4C_{11}H_{20}N_6O_3$ 703.01	27.25	27.34	3.37	3.30	20.19	19.92	8.99	8.38	-	-
L_2Ni	$NiCd(SCN)_4C_{15}H_{14}N_4O_5$ 748.75	27.37	27.35	3.81	330	19.24	19.93	-	-	8.91	8.35

Table 2: Characteristic IR bonds of the ligands and their complexes

Sym.of Comp. cm^{-1}	C-H Azomethin cm^{-1}	C-H Alp. cm^{-1}	HC=N cm^{-1}	C=C cm^{-1}	O-H cm^{-1}	C=O cm^{-1}	NH cm^{-1}	C-N in M-SCN cm^{-1}	S-C in M-SCN cm^{-1}	C-N in M-SCN-M cm^{-1}	M←N cm^{-1}	M-NSC cm^{-1}	M-SCN cm^{-1}
L_1	2890	-	1620	1598	3321	1690	3377	-	-	-	-	-	-
L_1Co	2885	-	1603	1570	3346	1692	3350	2075	750	2150	525	434	415
L_1Ni	2883	-	1605	1575	3350	1998	3345	2073	745	2145	522	440	420
L_2	2887	2951	1641	1537	-	1690	3325	-	-	-	-	-	-
L_2Co	2890	2954	1635	1560	-	1699	3327	2080	747	2140	535	450	425
L_2Ni	2887	2955	1633	1555	-	1694	3320	2075	745	2135	533	445	423

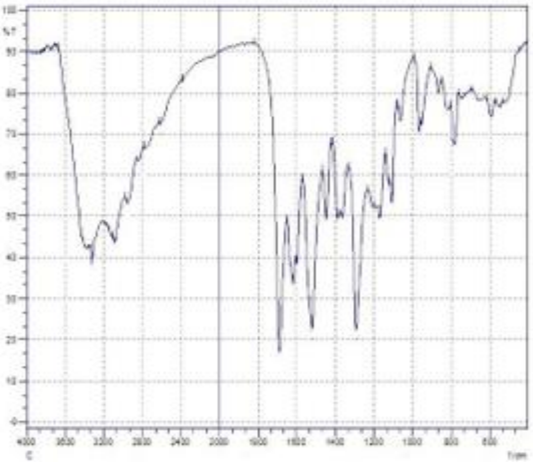


Figure 1 : IR Spectrum of the ligand L_1

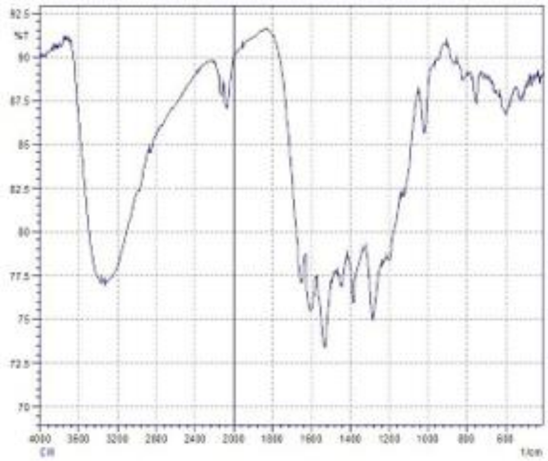


Figure 2: IR Spectrum of the complex L_1Co

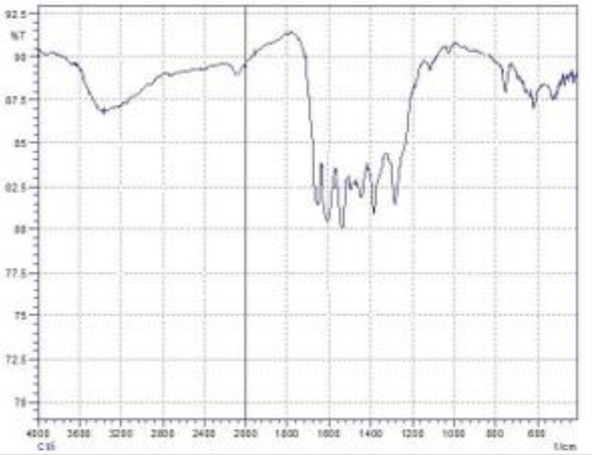


Figure 3 : IR Spectrum of the complex L_1Ni

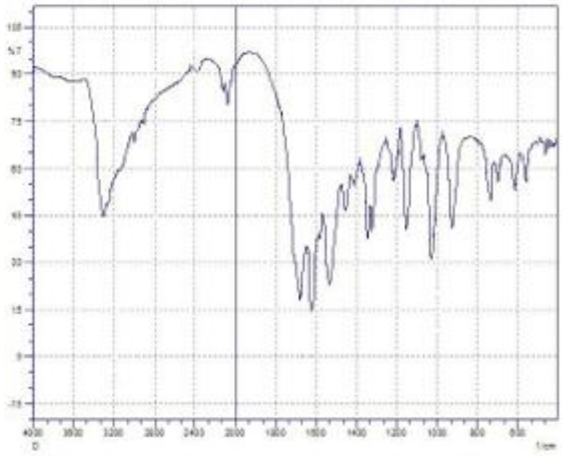


Figure 4 : IR Spectrum of the ligand L_2

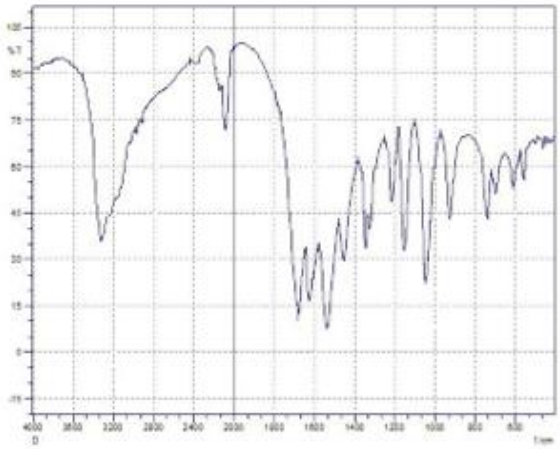


Figure 5 : IR Spectrum of the complex L_2Co

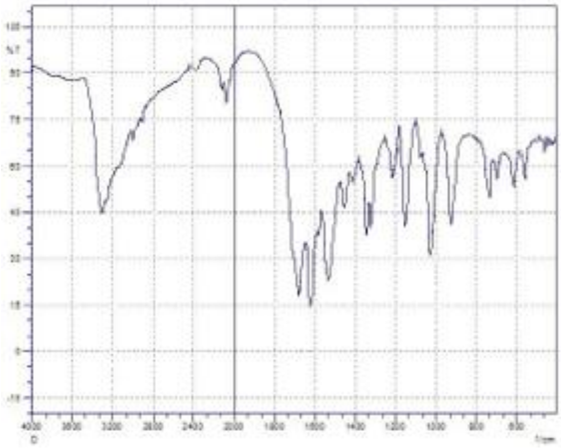


Figure 6 : IR Spectrum of the complex L_2Ni

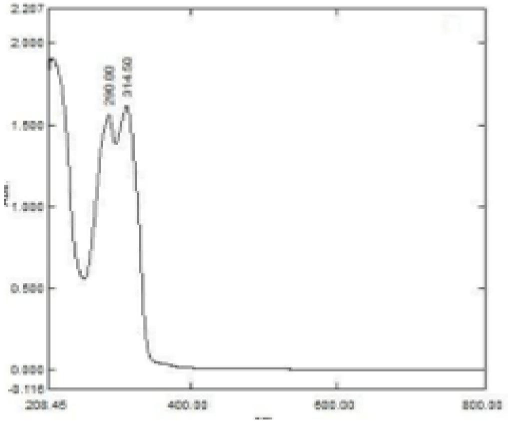


Figure 7: UV -Visible spectrum of the ligands L_1

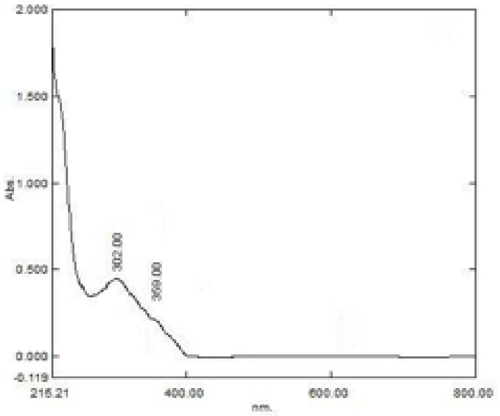


Figure 8: UV -Visible spectrum of the ligands L_2

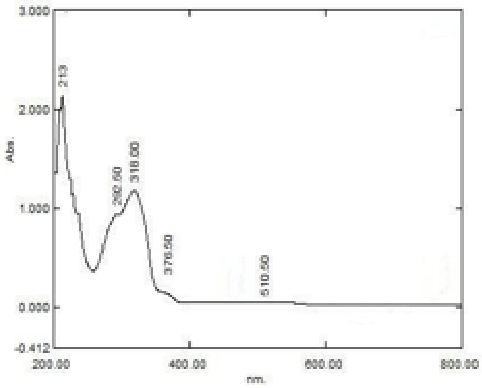


Figure 9: UV -Visible spectrum of the complex L_1Co

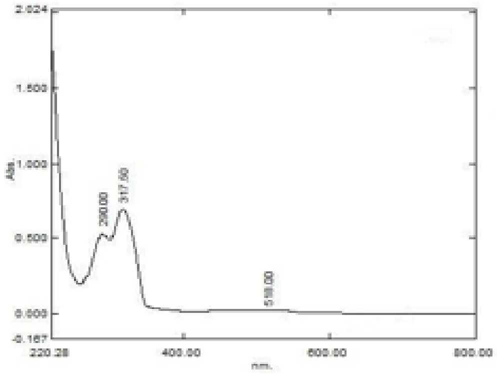


Figure 10: UV -Visible spectrum of the complex L_1Ni

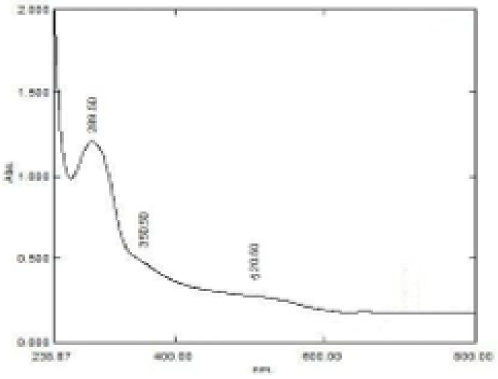


Figure 11: UV -Visible spectrum of the complex L_2Co

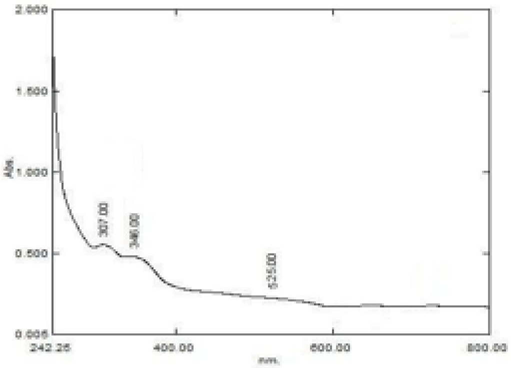


Figure 12: UV -Visible spectrum of the complex L_2Ni

Table (3): Chemical shifts of ^{1}HNMR and ^{13}CNMR for the ligands

Ligand	^{1}HNMR	^{13}CNMR
	Chemical shifts (ppm)	Chemical shifts (ppm)
L_1	10.61-10.56(2H, OH), 10.09(2H, NH), 6.66-7.36(6H, Ar-H), 8.48(2H,HC=N-)	C1(154.97) ,C2(146.26) , C3(126.98) , C4(120.02) , C5(115.63) , C6(147.19) , C7(144.53) , C8(114.92)
L_2	10.55(2H,NH), 3.69-30.44(16H,CH_2) ,8.01(2H,-HC=N-)	C1(155.42), C2(137.89), C3(46.44), C4(65.24)

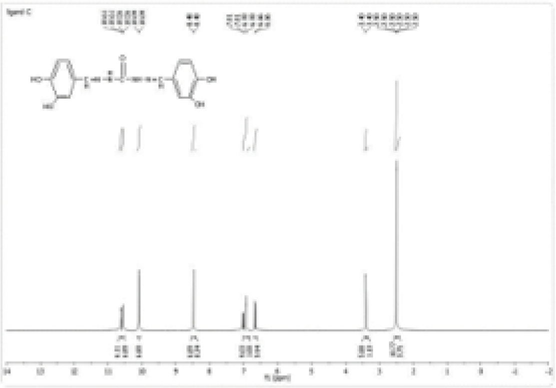


Figure 13: ^{1}HNMR spectrum of the ligand

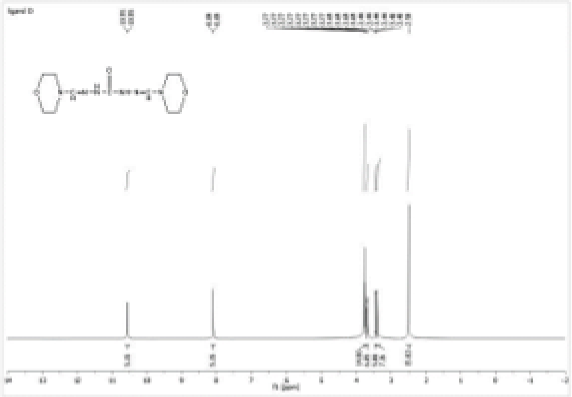


Figure 14: ^{1}HNMR spectrum of the ligand

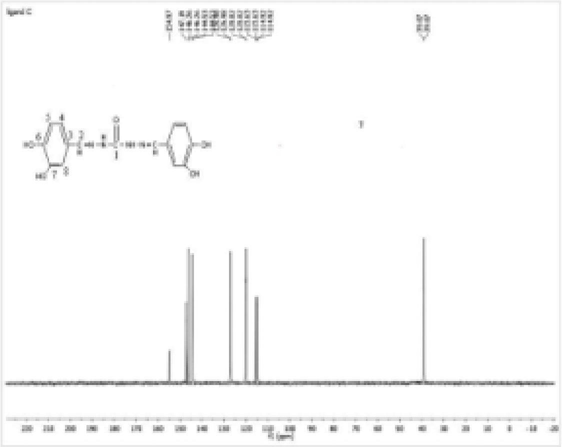


Figure 15: ^{13}CNMR spectrum of the ligand

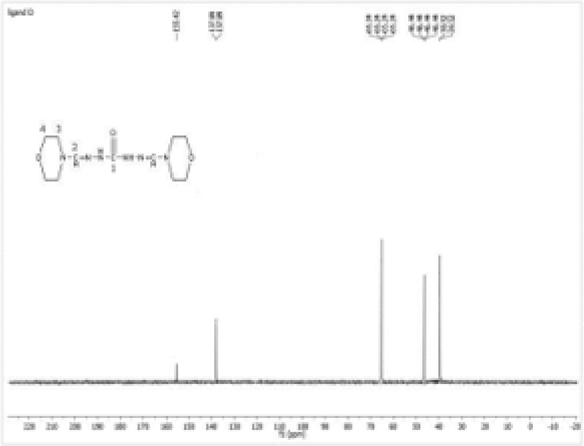


Figure 16: ^{13}CNMR spectrum of the ligand

Table (4): Molar conductivity and magnetic moment of the complexes

Sym. Of Complex	Formula of Complex	μ_{eff}	Molar Conductivity Ohm^{-1}cm^1/mol	Magnetic Properties	Hybridization and geometry
L_1Co	$CoCd(SCN)_4C_{15}H_{14}N_4O_5$ 748.99	4.413	16.9	Paramagnetic	sp^3 (tetrahedral)
L_1Ni	$NiCd(SCN)_4C_{15}H_{14}N_4O_5$ 748.75	1.132	18.3	Diamagnetic	dsp^2 (square planar)
L_2Co	$CoCd(SCN)_4C_{11}H_{20}N_6O_3$ 703.01	4.243	21	Paramagnetic	sp^3 (tetrahedral)
L_2Ni	$NiCd(SCN)_4C_{11}H_{20}N_6O_3$ 702.77	1.105	19.2	Diamagnetic	dsp^2 (square planar)

Table (5) : biological activity data of the ligands and their complexes

Compound	Diameter of inhibition zone (mm)			
	Bacteria species		Fungi species	
	Staphylococcus	E.coli	Candida	Aspergillus
L_1	36	30	12	34
L_2	25	31	16	33
L_1Co	32	30	37	52
L_2Co	33	26	36	38
L_1Ni	35	30	34	40
L_2Ni	31	28	22	20

CONCLUSION

Schiff base ligands derived from carbohydrazide with 4-isopropyl benzaldehyde or 4-diethylamino benzaldehyde were prepares and reacted with MM` $(SCN)_4$[M=$Co^{+2}$,$Ni^{+2}$, M`=Cd^{+2}] These compounds were identified by analytical and spectral techniques. It was observed that these ligands. were bidentate, and complexes had coordination number equal four. All ligands and complexes had good antibacterial and antifungal activity

REFERENCES

1. A.A.Osowole,A.C. Ekennia and B.O.Achugbu, *Res.Rev.J. Pharm.Anal.*, **2**,1, 2013
2. S. M. Morgan, A. Z. El-Sonbati and H. R. Eissa, *J. Mol. Liq.*,**240** , 752 ,2017.
3. S. Rekha and K. R. Nagasundara, *Indian J. of Phys. Chem. ,* **45**, 2421, 2006
4. S.M. Abdallah , G.G-Mohammed , M.A.Zayad and M.S. Abou El-Ela , *Spectrochim. Acta* , **73**, 833, 2009
5. M.M. H. Khalil, M. M. Aboady and R. M. Ramadan, *Spectrochim. Acta*, **61**, 157, 2009

A. Kilic, E. Tas, B. Deveci and I.Yilmaz, *Polyhedron*, **26**, 4009, 2007

6. M.Y. Kadhum and B. J. Al-Musawi , *Adv. Appl. Sci. Res.*, **6** (10), 120, 2015
7. M.Y. Kadhum , S.R.Kareem and S.Q. Badr, *International J. Sci and Res.*, **7**, 320, 2018
8. M.A. Enad, M.Y.Kadhum and A.S. Abdulnabi , *J. Global Pharma. Tech.*, **12**, 651, 2020
9. M.Y. Kadhum , S. R. Kareem and S. Q.Badr, *Inter. J. Sci. and Res.* , **7**, 320 , 2018 .
10. J. Gou, Yang S. Li , L. Zhao, H. Gao and J. Cui , *polyhedron*, 201, 2021
11. R. J. Clark and C.S. Williams , *Spectrochim .Acta* , **22**, 1081 , 1966
12. J. Lewis , R. Nyholm and P.wasmith. , *J. Chem. Soc.* , 4590 ,1961

A. Sabatini and I. Bertini, *Inorg.Chem.* , **4** , 959 (1965)

13. A.A. Osowole, *E. J. chemistry*, **5**, 130, 2008
14. O.A. El-Gammal, F.Sh. Mohamed, G.N. Rezk and A.A. El-Bindary, *J. Molec. liquids*, 330, 2021
15. R.V. Sakthivel, P. Sankudevan, P. Vennila and G. Serdaroglu, *J. Molec. Structure*, **1233**, 130097, 2021