

Preparation, Spectral Characterization of New Mixed Ligand Complexes with Dithiocarbamate

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الخلاصة

تضمن البحث تحضير عدد من معقدات مختلطة الليكاند لايونات الكوبلت (II)، النيكل (II)، النحاس (II) والارصين (II) مع مزيج الليكاندين 8-هايدروكسيكويولين وثنائي ثايوكارباميت ذات الصيغة [M(dtc Q)]. شخّصت هذه المعقدات باستخدام تحليل العناصر، التوصيلية المولارية حيث تبين إن سلوك المعقدات غير الكتروليتية، الأشعة تحت الحمراء، الأشعة فوق البنفسجية والعزم المغناطيسي وقد اقترح الشكل رباعي السطوح لكل من المعقدات المحضرة.

Abstract

The preparation of new Co(II), Ni(II), Cu(II) and Zn(II) complexes with mixed two ligands including 8-hydroxyquinoline and dithiocarbamate with molecular formula [M(dtc Q)]. The resulted complexes have been characterized using elemental analysis, molar conductance measurement indicates a nonelectrolyte behavior, Infrared spectra, UV-VIS spectroscopy and magnetic moments. The suggested structure for all complexes were tetrahedral formula.

Key Words: mixed ligand complexes, dithiocarbamate, spectral data.

Introduction

Dithiocarbamate are versatile compound wide range of chemistry. An extremely large number of dithiocarbamate complexes with transition and non-transition metal ions have been reported^[1-3] and chelating agents with diverse application in industry, agriculture and medicine^[4,5]. Mixed ligand complexes play key roles in biological, environmental systems and also act as catalyst in reactions of industrial importance^[6,7]. Hence a large number of mixed ligand complexes with various transition metals are known^[8-10]. Several research papers reported the synthesis and characterization of metal complexes derived from 8-hydroxyquinoline^[11-12A].

Experimental

Anal grade chemical reagents supplied by B.D.H, Merck and Fluke were used without further purification.

Instruments

UV-Vis spectra were recorded on (Shimadzu UV-160 A) Ultra Violet –Visible spectrophotometer, IR- spectra were taken on a (Shimadzu , FTIR-8 400 S) Fourier Transform Infrared Spectrophotometer ($4000-400$) cm^{-1} with samples as discs. Elemental analysis (C.H.N) was (EURO3000 Single), Conductivities were measured for 10^{-3}M of complexes in DMSO at 25°C using (Digits conductivity meter WTW,720), Metal contents complexes were determined by atomic absorption (A.A) technique using Atomic Absorption spectrophotometer-5000, Perkin-Elmer.

Perparation of Potassium dithiocarbamate

Dithiocarbamate ligand has been prepared according to literature method ^[13].

Preparation of complexes [M (dtc)(Q)]

The metal solution of metal salt [0.75 m mole] in 10ml ethanol was stirred for 10 minutes. The ligand solution (0.2 g, 0.77 mmole in 10ml ethanol) after adjusted to pH=9 using few drops of KOH solution was added to the metal solution. Finally a solution of 8-hydroxy quinolone (0.11, 0.75 m mole) in 10 ml ethanol was also added to the above metal solution. The resulting mixture was heated under reflux for 2hrs .Then the mixture was filtered and the precipitate was washed with an excess of ethanol and dried at room temperature during (24 hrs.) A mustard solid was obtained.

Results and Discuses

The complexes are solid, stable in atmospheric condition and non hydrscopic .All these complexes are insoluble in common organic solvents. The molar conductance measurements of complexes in DMSO solution lie in the range $(24 - 8) \text{ s cm}^2\text{mol}^{-1}$, indicating their non-electrolyte behavior. The analytical and some physical properties of complexes are listed in Table 1.

Table 1: Analytical and some physical properties of complexes.

Comp.	Empirical formula	MW. g/m	Yield %	color	Found(Calc) %				
					M%	C	H	N	S
[Co(dtcQ)]	$\text{CoC}_{26}\text{H}_{24}\text{N}_2\text{O}_3\text{S}_2$	535.54	66.27	Dark	8.76	55.74	4.72	3.72	17.34
				green	(8.96)	(55.91)	(4.97)	(3.84)	(17.56)
[Ni(dtcQ)]	$\text{NiC}_{26}\text{H}_{24}\text{N}_2\text{O}_3\text{S}_2$	535.30	53.55	green	10.80	58.21	4.60	5.25	11.88
				green	(10.96)	(58.34)	(4.52)	(5.23)	(11.98)
[Cu(dtcQ)]	$\text{CuC}_{26}\text{H}_{24}\text{N}_2\text{O}_3\text{S}_2$	540.16	53.04	green	11.66	57.70	4.36	5.30	11.94
				green	(11.76)	(57.81)	(4.48)	(5.19)	(11.87)

[Zn(dtcQ)]	ZnC ₂₆ H ₂₄ N ₂ O ₃ S ₂	542.02	47.82	White	12.20 (12.07)	57.58 (57.61)	4.55 (4.46)	5.02 (5.17)	11.90 (11.83)
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IR- Spectroscopy

The assignment of the infrared spectra bands of ligand and their complexes are listed in Table 2.

The ν (N-CSS) band order intermediate between a single bond (1350-1250) cm^{-1} and double bond (1690-1640) cm^{-1} , in the complexes this band is not the big change compared with free ligand. The second region of ν CS₂ was observed in the (1034-997) cm^{-1} the a positive shift in comparison to the corresponding band in the free ligand indicates that the dithiocarbamate ligand coordinates with the metal through sulfur atoms [14,15]. The infrared of prepared complexes have shown some new bands at (380-360), (497-460) and (597-503) cm^{-1} due to the formation of ν (M-S), ν (M- N) , ν (M-O) bands respectively [16] in the resulting complexes. Show Figures 1,2,3,4,5.

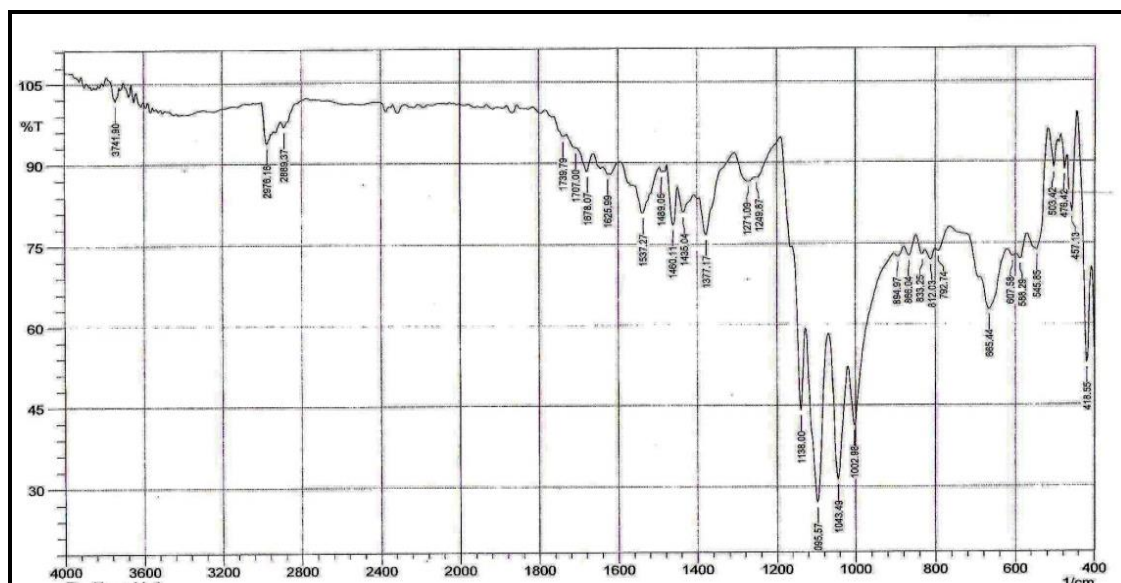


Fig. 1: FTIR spectra of the ligand(dtc).

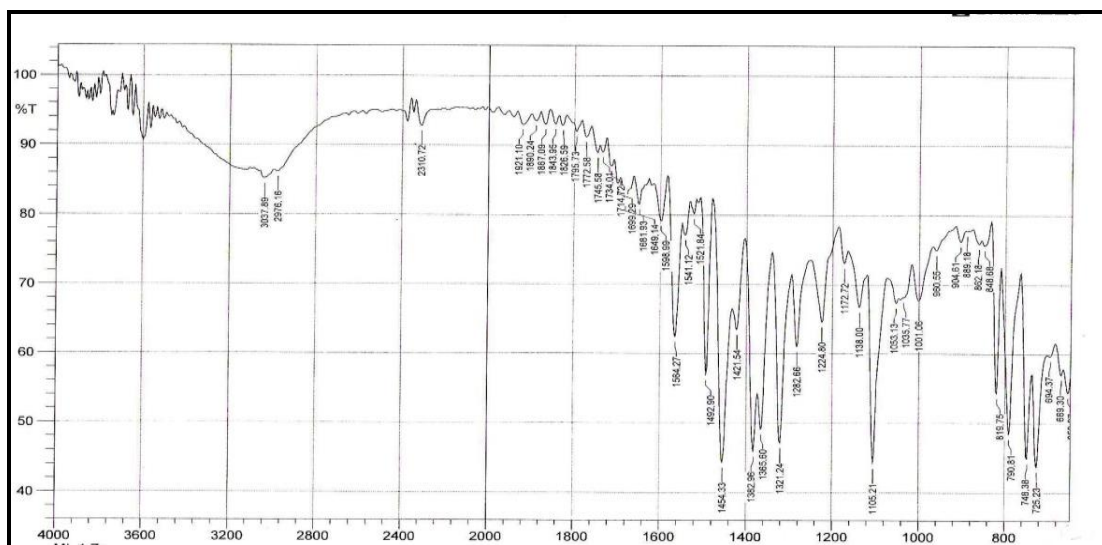


Fig. 2: FTIR spectra of the Co(II) complex.

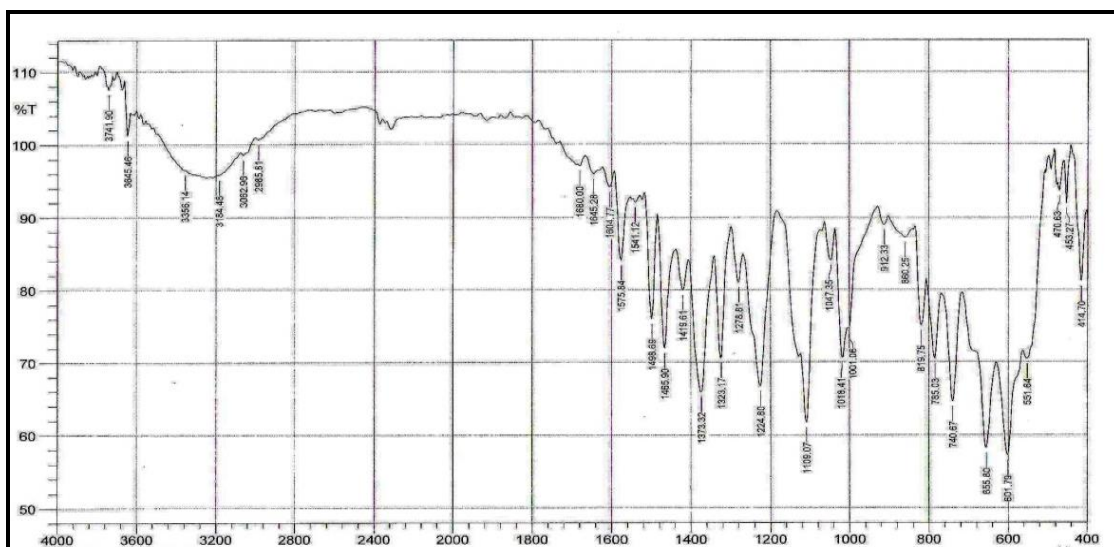


Fig. 3: FTIR spectra of the Ni(II) complex.

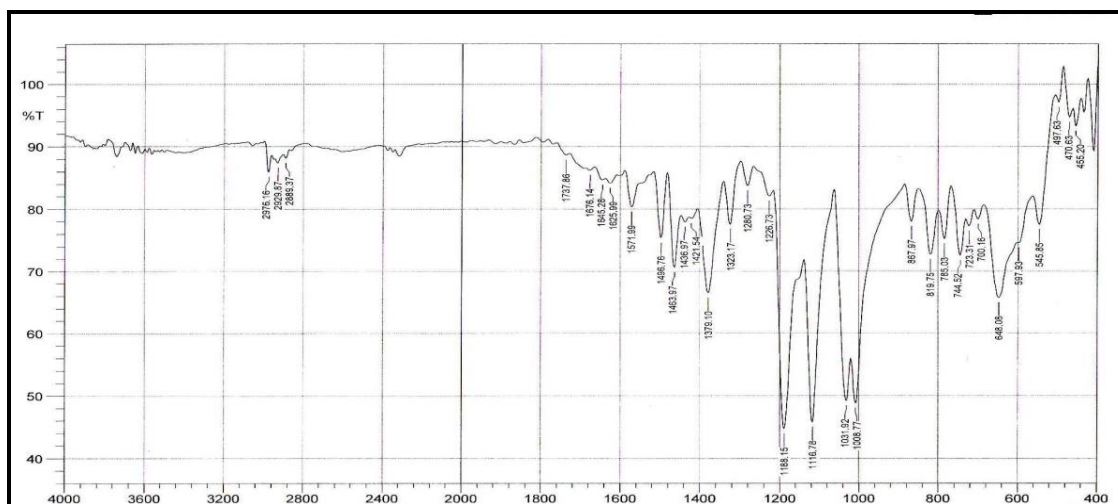


Fig. 4: FTIR spectra of the Cu(II) complex.

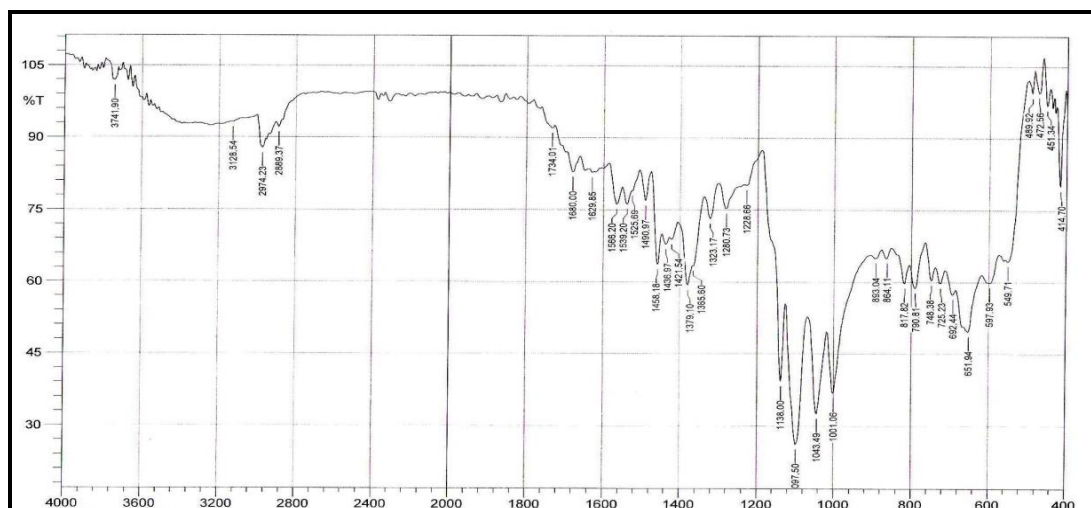


Fig. 5: FTIR spectra of the Zn(II) complex.

Table 2: The characteristic bands of Infrared spectra of the ligand and their complexes.

No	Comp.	$\nu_{\text{ar}}(\text{C-H})$	$\nu_{\text{al}}(\text{C-H})$	$\nu(\text{C=O})_{\text{di}}$	$\nu(\text{C=C})$	$\nu(\text{N-CS}_2)$	$\nu(\text{CS}_2)$
1	dtc	3059w	2954s	1625m	1537s	1460s	1001s 1043s
2	[CodtcQ]	3167w	2978w	1665m	1568m	1458s	997s 1033m
3	[NidtcQ]	3184w	2985w	1665m	1576s	1465s	1001w 1018s
4	[CudtcQ]	2978w	2929w	1645w	1571m	1463s	1008s 1031s
5	[ZndtcQ]	3037w	2976w	1642w	1564m	1458s	1001s 1043s

Electronic spectra and Magnetic moment

The electronic spectra of the ligand and complexes display the absorption bands listed in Table 3. The ligand show bands between (252-320)nm due to intraligand raised from $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition located on sulfur atoms (17). The electronic spectrum of Co(II) complex show a band at (277,252,366)nm may be due to $\pi \rightarrow \pi^*$ and charge transfer, the other bands (614)nm may be attributed to $^4A_{2(\text{F})} \rightarrow ^4T_{1(\text{P})}$. The magnetic moment value (4.67 B.M).

The electronic spectrum of Ni(II) complex show band at (269.305.345)nm due to intra ligand and charge transfer, the other bands at (407,745)nm may be attributed to $^3T_{1(\text{F})} \rightarrow ^1T_2$, $^3T_{1(\text{F})} \rightarrow ^3T_{1(\text{P})}$. The magnetic moment value (3.136 B.M).

The electronic spectrum of Cu(II) complex show a band at (269,353)nm may be due to $\pi \rightarrow \pi^*$ and charge transfer, the other bands (406)nm may be attributed to $^2T_2 \rightarrow ^2E_2$ (18). The magneticmoment value (2.78 B.M). Finally complex of Zn(II) exhibited bands assigned

to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and charge transfer and do not display any d-d transition. Show **Figures 6,7,8,9.**

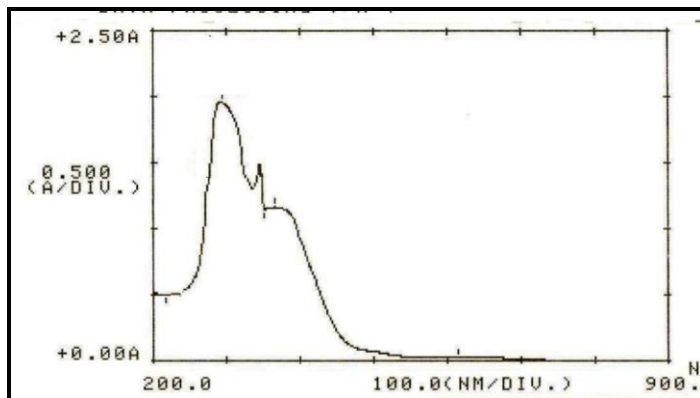


Fig. 6:Electronic Spectrum of Co(II) complexes.

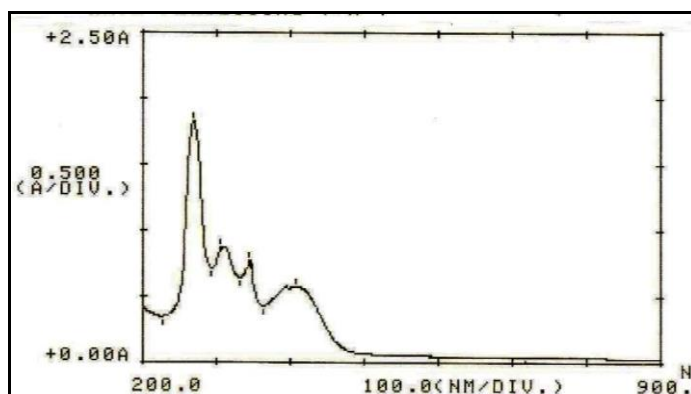


Fig. 7: Electronic Spectrum of Ni(II) complexes.

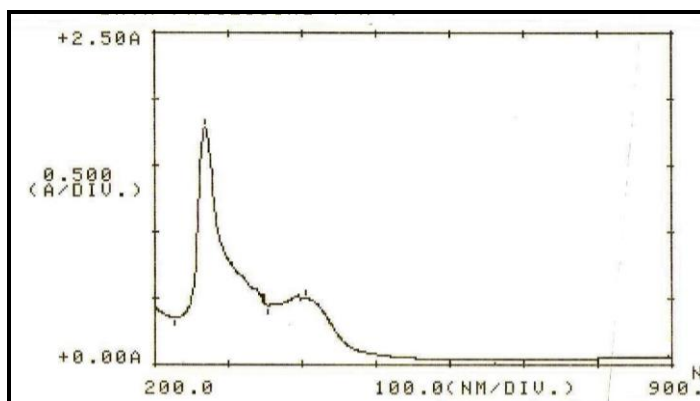


Fig. 8:Electronic Spectrum of Cu(II) complexes.

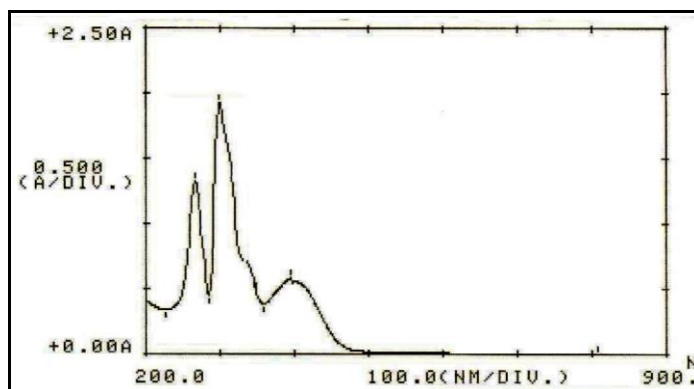


Fig. 9: Electronic Spectrum of Zn(II) complexes.

Table 3:UV-Vis spectra of free ligand and their complexes in DMSO solution.

Comp.	Band Position λ_{nm}	Wave number (cm^{-1})	Assignment	Suggested geometry
dtc	252	33333	Intra-ligand	
	267	32573	$\pi \rightarrow \pi^*$	
	320		$n \rightarrow \pi^*$	
[CodtcQ]	277	36101	Intra-ligand	Tetrahedral
	352	28409	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$	
	366	27322	C.T	
	614	16286	$^4A_{2(F)} \rightarrow ^4T_{1(P)}$	
	269	37174	Intra-ligand	
[NidtcQ]	305	32786	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$	Tetrahedral
	345	28985	C.T	
	407	24570	$^3T_{1(F)} \rightarrow ^3T_{2(P)}$	
	745	13422	$^3T_{1(F)} \rightarrow ^3T_{1(P)}$	
[CudtcQ]	269	37174	Intra-ligand	Tetrahedral
	353	28328	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$	
	406	24630	$^2T_2 \rightarrow ^2E_2$	
[ZndtcQ]	269	37174	Intra-ligand	Tetrahedral
	301	33222	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$	
	396	25252	C.T	

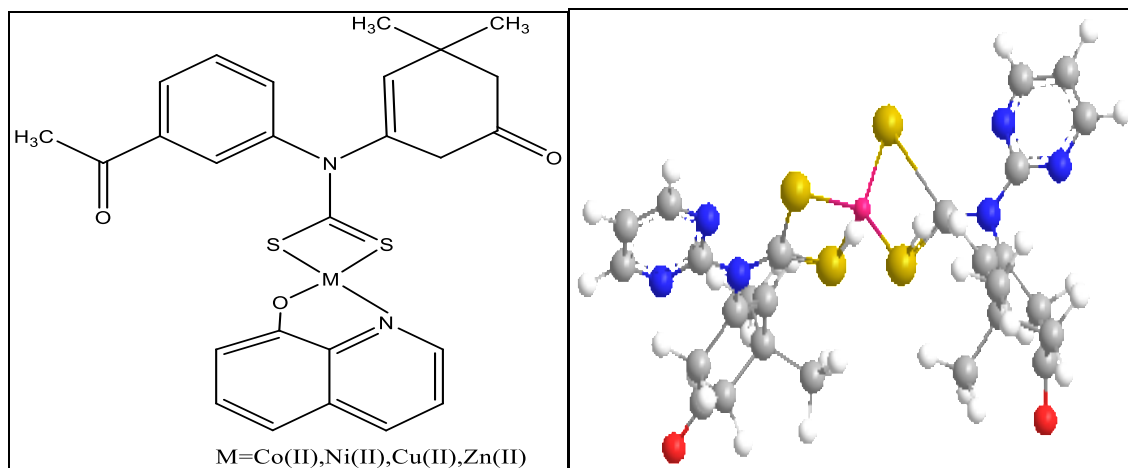


Fig. 6: Suggested structure of the complexes

Reference

- 1) Kom – Bei S, Sheng –Ting L , Shie –Ming .Pand Ming –Chu. C, [1995] , J,Inorganic .ChimicaActa ,(229),P153-163.
- 2) 2-Venu gopal.K ,Siva Jyothi.P ,Ashok GajapathiRaju.P, Rameshbabu.K and Sreermulu.J,[2013], J, Chemical and pharmaceutical Research,5(6),p50-59.
- 3) Venugopal.K, Musthaq Ahammed.M, Jaya Raju.A. Rameshbabu.K, NoorjahanBegum.T and Sreermulu.J,[2014], J,Unique Res. chem,2(1),p 8-15.
- 4) Hulanicki.A,[1967],Talanta,14,p 1371-1392.
- 5) Coucouvanis.D,[1970],Prog.Inorg.Chem,11,p233-371.
- 6) Ajay.RP, Kamini.JD, Sambhaji.SR, Vishwanath.RP and Rama.SL,[2012].J.Pharm.Res.chem ,4(2),p1413-1425.
- 7) Bruce MR, Ponaldo P,[1974],J.Inorg.Nucl.chem.39(7),p 1279-1982.
- 8) Pastorek R, Kamenicek J, Brezina F ,HamrusovaM, Sindelar Z and Lasovsky, [1993], J.chem.Papers,47(4),p 210-214.
- 9) Maria L, MonirU, Hadjikostas C C, HarrisP, George P, Stergion A and Vasiliki A, [1997], J,Z.anorg.all.chemi,623,p 1983-1990.
- 10) BharathiK, Vijayanthimala R and Nivedha K R,[2015],J,IOSR of Applied chem.,8(4),p 46-51.
- 11) Mahmoud M, Zinab H and Abeer A,[2004],J,Chinse chemical of Society,51,p 901-915.
- 12) Yuvraj S,Rakesh C and Rajesh W,[2009],J,Acta Polish Plamaceutical Society,66(1),p 45-50.
- 13) Al-Saada A S, Al-Kafajy H Aand Numan A T ,[2015],J, Multf Materials and Photo,6(1),p 21-26.
- 14) Kellner R,Nikolov G S and Trendafilova ,[1984],J,Inorg.chim Acta,84,p 233.
- 15) Nakamoto K, [1997]Infrared and Raman Spectra of Inorganic and Coordination Compounds,(5thED),John Wiley and Sons, New York.
- 16) Ferraro L R,[1977],Low Frequncy Vibration of Inorganic Coordination Compounds, plenum press,New York.
- 17) Leka Z, Gruij S A,Tesic Z, Lukie S, Skuban S and Trrifunovic S, [2004]J.Serb.chem.Soc,69(2),p 137.
- 18) Lever A B,[1984],Inorganic spectroscopy; Elsevier, Amsterdam.