

Synthesis and Characterization of Some Mixed Ligand Complexes of Quinaldic Acid and α -Picoline with Some Metal Salts

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الخلاصة

يتضمن البحث تحضير وتشخيص بعض المعقدات الفلزية التي تحوي على ليكاندات مختلطة لحمض الكوينالديك (QuinH) و α - بيكولين (α -Pic) وقد درست وشخصت بالطرائق الطيفية (الاشعة تحت الحمراء والاشعة المرئية - فوق البنفسجية) والتوصيلية المولارية والحساسية المغناطيسية وتعيين نسبة الفلز في المعقدات باستخدام تقنية الامتصاص الذري. ومن نتائج هذه الدراسات التشخيصية اقترح الشكل الثماني السطوح لهذه المعقدات مع اعطاء الصيغة العامة لهذه المعقدات وكما يأتي: $[M(Quin)_2(\alpha-Pic)_2].XH_2O$ اذ $M^{+2} = (Mn, Co, Ni, Cu, Zn, Cd, Hg)$ و $X = 2$ ماعدا معقدات ابوني Co^{+2} و Hg^{+2} حيث $X = 0$ ، $Quin^- =$ ايون الكوينالديك، $\alpha = (\alpha-Pic)$ بيكولين. حيث أثبتت النتائج أن حامض الكوينالديك الفاقد البروتون والمنحول الى ايون الكوينالديك ($Quin^-$) باستعمال (KOH) يسلك كليكاند ثنائي السن، اذ يرتبط عن طريق ذرة الاوكسجين في مجموعة الكربوكسيل وذرة النتروجين في حلقة البيريدن، بينما α - بيكولين يسلك كليكاند احادي السن اذ يرتبط من خلال ذرة النتروجين في حلقة البيريدن.

الكلمات المفتاحية: ليكاندات مختلطة، حامض الكوينالديك، α - بيكولين، المعقدات الفلزية.

ABSTRACT

Some metal ions (Mn^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} and Hg^{+2}) complexes of quinaldic acid (QuinH) and α -picoline (α -Pic) have been synthesized and characterized on the basis of their , FTIR, (U.V-Vis) spectroscopy, conductivity measurements, magnetic susceptibility and atomic absorption. From the results obtained the following general formula has suggested for the prepared complexes $[M(Quin)_2(\alpha-Pic)_2].XH_2O$ where $M^{+2} = (Mn, Co, Ni, Cu, Zn, Cd$ and $Hg)$, $X = 2$, $X = zero$ for (Co^{+2} and Hg^{+2}) complexes, ($Quin^-$) = quinaldate ion, (α -Pic) = α -picoline. The results showed that the deprotonated ligand (QuinH) by using (KOH) coordinated to metal ions as bidentate ligand through the oxygen atom of the carboxylate group ($-COO^-$) and the nitrogen atom of the pyridine group. The α -picoline coordinates as amonodentate through the nitrogen of the pyridine group.

Key words: Mix ligand, quinaldic acid, α -picoline, complexes.

INTRODUCTION

Quinaldic acid ($C_{10}H_7NO_2$) and its derivatives used as inhibitors for corrosion of steel [1] and derivatives of quinoline and its isosters are remarkable compounds with many different kinds of biological effects. A number of quinoline related compounds expressed antibacterial [2,3]. Dylan and coworker's [4] were treatment of iron (II) chloride or iron (II) bromide with 2 equivalent of sodium quinaldate yields the coordinatively unsaturated mononuclear iron (II) quinaldate complexes $Na[Fe^{II}(qn)_2Cl].DMF$ and $Na[Fe^{II}(qn)_2Br].DMF$ (qn=quinaldate,

DMF=N,N-dimethylformamide) respectively. Abhishek and coworker's [5] were studied and synthesized isomeric complexes of $[\text{Ru}^{\text{II}}(\text{trpy})(\text{L})\text{Cl}]$, ($\text{trpy} = 2,2':6', 2''\text{-terpyridine}$ and $\text{HL} = \text{quinaldic acid}$). Eizbleta and coworker's [6] were studied the complexes of VO^{IV} ion with picolinate and quinolate derivatives formation in aqueous solution and in the solid state. We have investigated in this paper, the preparation and properties of some metal ion complexes with quinaldic acid and α -picoline.

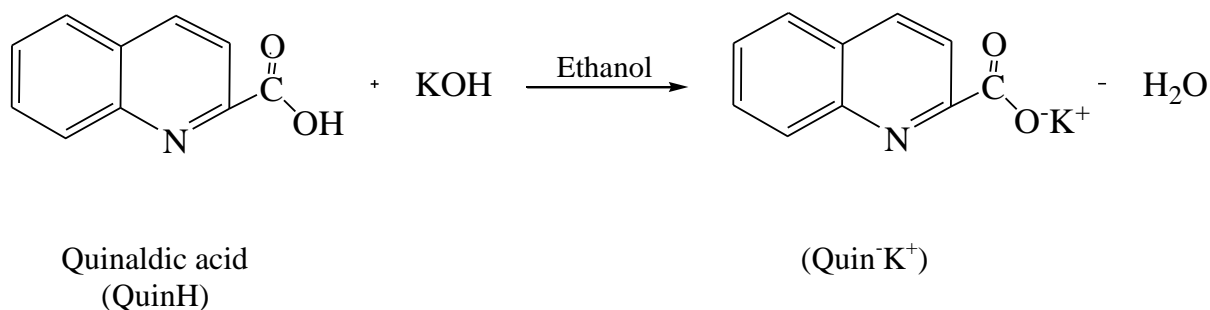
MATERIALS AND METHODS

Metal salts ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and HgCl_2) were obtained from Fluka, Merck in high purity, ligand (quinaldic acid) from (BDH) and (α -picoline) Merck. Conductivity measurements were carried out using Philips PW.Digital-meter. FTIR spectra in the reign ($4000\text{-}400$) cm^{-1} were recorded on (Shimadzu FTIR-8300) infrared spectrophotometer as KBr discs. The (U.V-Vis) spectra were recorded using (Shimadzu U.V- Vis 160A), (U.V-Vis) spectrophotometer in dimethyl sulphoxide solution (10^{-3} M). Metal contents of the complexes were determined by Atomic absorption technique by using Shimadzu (AA680G), Atomic absorption spectrophotometer. The magnetic moments (μ_{eff} B.M) were calculated on Faraday method by using (Balance Magnetic Susceptibility Model MSBMKT). Melting points were determined by using (Stuart-melting point apparatus).

General method for the synthesis

a) Potassium quinaldate ion (Quin^-K^+)

(0.34g, 2mmole) of (QuinH) dissolved in (10ml) of ethanol and added to (10ml) of ethanolic solution containing (0.112g, 2mmole) of KOH. The Quinaldic acid was deprotonated according to the following reaction:



b) Synthesis of complexes

An aqueous solution of the metal salts contains (0.198g , 0.237g , 0.237g , 0.170g , 0.136g , 0.21g and 0.271g) (1mmole) of

($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and HgCl_2) respectively were added to the solution of the ligand ($\text{Quin}^- \text{K}^+$) (0.346g, 2mmole) in ethanol, the mixture was stirred for half an hour at room temperature. Complexes were separated adding an excess of α -picoline (2mole) (1-4ml) and treating the solution with diethyl ether until is completed precipitation. The precipitate was recrystallized from ethanol and dried at (50 °C)[7].

RESULTS AND DISCUSSION

The isolated complexes were crystalline, solids, soluble in some of common solvents such as dimethyl formamide (DMF), dimethyl sulphoxide (DMSO). They are relatively thermally stable, the conductivity measurements in DMSO indicated the non-electrolyte behavior; Table-1 includes the physical properties. The analytical data confirmed the (1:2:2) (Metal:(Quin):(α -pic)) composition of the complexes. The magnetic measurements (μ_{eff} B.M) for the complexes are also listed in Table-1.

Spectral studies

FT-IR spectra

In order to get further information about the coordination behavior of the ligands (QuinH) and (α -pic) with metal ions, comparisons of the infrared spectra of the free ligands and their complexes are done Table-2 describes the important absorption and assignment. The strong absorption band at (1620) cm^{-1} in the spectrum of the free ligand (QuinH), Figure-1 assigned to $\nu(\text{COO})_{\text{asym}}$. and another strong absorption was noticed at (1317) cm^{-1} could be explained as $\nu(\text{COO})_{\text{sym}}$. another band at (1387) cm^{-1} was assigned to $\nu(\text{C-N})$ [8,9]. The spectrum of free (α -picoline) showed band at (1613) cm^{-1} was assigned to $\nu(\text{C=N})$ [10].

The spectra of the complexes

Exhibited a marked differences the in absorption band belonging to the stretching vibration of $\nu(\text{C-N})$ found in the range between (1404-1438) cm^{-1} which shifted to higher frequencies by (17-51) cm^{-1} suggesting the possibility of the coordination of ligand (Quin^-) through the nitrogen atom in the ring [11]. Absorption assigned for $\nu(\text{COO})_{\text{sym}}$. was noticed at range (1375-1465) cm^{-1} shifted to higher position by (58-148) cm^{-1} while the band caused by $\nu(\text{COO})_{\text{asym}}$. appeared between (1506-1568) cm^{-1} shifted to lower frequencies by (114-52) cm^{-1} which indicates the coordination of the carboxylic group to the central metal ion [12,13]. The stretching vibration band $\nu(\text{C=N})$ appeared in the range (1462-1608) cm^{-1} shifted to lower frequencies by (151-5) cm^{-1} which

means that the nitrogen atom of α -picoline was involved in the coordination[14]. Absorption bands in the (410-468) cm^{-1} region are considered to be due to metal-nitrogen $\nu(\text{M-N})$ vibrations whilst those occurring around (442-501) cm^{-1} are through to a wise from metal-oxygen (M-O) vibrations [11,13], Figure-2 showed the FTIR spectrum of $[\text{Hg}(\text{Quin})_2(\alpha\text{-Pic})_2]$.

Electronic spectra

The absorptions and assignments related to the ligands and their complexes are listed in Table-3. The ligand, Figure-3 exhibited an absorption band in (U.V) region at wave number (44052) cm^{-1} which may be attributed to ($n \longrightarrow \pi^*$) transition. Free α -picoline, Figure-4 showed absorption band at (48542) cm^{-1} which was expressed as the ($n \longrightarrow \pi^*$)[9,15].

The spectra of the complexes

- $[\text{Mn}(\text{Quin})_2(\alpha\text{-Pic})_2].2\text{H}_2\text{O}$ (d^5)

The spectrum of this complex showed two absorption at (34246) cm^{-1} , (23803) cm^{-1} and (32154) cm^{-1} which may be attributed to (C.T) and ${}^6\text{A}_{1g} \longrightarrow {}^4\text{T}_{2g}(\text{D})$ transitions respectively[16].

- $[\text{Co}(\text{Quin})_2(\alpha\text{-Pic})_2]$ (d^7)

The spectrum of this complex exhibited bands at (33444) cm^{-1} , (30864) cm^{-1} , (15873) cm^{-1} and (11415) cm^{-1} which have been assigned to (C.T), ${}^4\text{T}_{1g} \longrightarrow {}^4\text{T}_1(\text{p})$, ${}^4\text{T}_{1g} \longrightarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g} \longrightarrow {}^2\text{T}_{2g}$ respectively[17] and the (B) found to be at (832.8) cm^{-1} , the ratio $\beta = B / B_0$ comes out to be at (0.857).

- $[\text{Ni}(\text{Quin})_2(\alpha\text{-Pic})_2].2\text{H}_2\text{O}$ (d^8)

The spectrum of this complex exhibited the following absorptions at (33333) cm^{-1} , (31948) cm^{-1} , (15625) cm^{-1} and (11363) cm^{-1} which have been assigned as (C.T), ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}(\text{P})$, ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}$ respectively and the (B) found to be at (898.23) cm^{-1} , the ratio $\beta = B / B_0$ comes out to be at (0.863)[18].

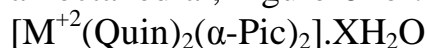
- $[\text{Cu}(\text{Quin})_2(\alpha\text{-Pic})_2].2\text{H}_2\text{O}$ (d^9)

The blue complex of Cu(II), Figure-5 gave two bands at (31746) cm^{-1} and (11312) cm^{-1} which may be attributed to (C.T) and ${}^2\text{E}_g \longrightarrow {}^2\text{T}_{2g}$ transitions respectively[19].

- [Zn(Quin)₂(α -Pic)₂].2H₂O , [Cd(Quin)₂(α -Pic)₂].2H₂O and [Hg(Quin)₂(α -Pic)₂] (d¹⁰)

The white complexes [Zn(Quin)₂(α -Pic)₂].2H₂O , [Cd(Quin)₂(α -Pic)₂].2H₂O and [Hg(Quin)₂(α -Pic)₂] confirmed the absence of any (d-d) transition [20-22]. The transitions with their assignment are summarized in Table-3.

According to spectral data as well as those obtained from elemental analysis, the chemical structure of the complexes may be suggested as an octahedral, Figure-6 for:



Where M⁺² = (Mn, Co, Ni, Zn, Cd and Hg)

X = 2, X = zero for (Co⁺² and Hg⁺²) complexes.

QuinH = quinaldic acid

α -Pic = α -picoline

Table-1: Physical properties of ligand and its complexes

Formula	Colour	M. Wt	M.p°C or dec.	Metal % (Calc.) (Found)	Molar conductivity (S.cm ² mole ⁻¹) in DMSO (10 ⁻³ M)	μ_{eff} (B.M)
[QuinH] [Ligand]	White	266	157-159	-	2.50	-
[Mn(Quin) ₂ (α -Pic) ₂].2H ₂ O	Yellow	620.9	240(dec.)	8.83 (8.51)	12.70	5.58
[Co(Quin) ₂ (α -Pic) ₂]	Violet	588.9	185	9.99 (11.14)	13.65	4.12
[Ni(Quin) ₂ (α -Pic) ₂].2H ₂ O	Green	624.7	340(dec.)	9.38 (9.79)	10.80	3.20
[Cu(Quin) ₂ (α -Pic) ₂].2H ₂ O	Blue	629.5	300(dec.)	10.08 (10.44)	6.8	1.72
[Zn(Quin) ₂ (α -Pic) ₂].2H ₂ O	White	631.4	260(dec.)	10.33 (10.55)	4.50	0.00
[Cd(Quin) ₂ (α -Pic) ₂].2H ₂ O	White	678.4	285(dec.)	16.55 (17.01)	18.3	0.00
[Hg(Quin) ₂ (α -Pic) ₂]	White	730.6	290(dec.)	27.43 (-)	13.7	0.00

Table-2: the characteristic infrared of the ligands (QuinH), (α -Pic) and their metal complexes

Complexes	$\nu(\text{C}=\text{N})$ α -Pic	$\nu(\text{OCO})_{\text{asym}}$	$\nu(\text{OCO})_{\text{sym}}$	$\Delta\nu(\text{COO}^-)$	$\nu(\text{C}-\text{N})$ Quin	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
[QuinH] [Ligand]	-	1620	1317	303	1387	-	-
α -Picoline	1613(s)	-	-	-	-	-	-
[Mn(Quin) ₂ (α -Pic) ₂].2H ₂ O	1508(m)	1558(s)	1464	94	1429(m)	450	499
[Co(Quin) ₂ (α -Pic) ₂]	1562(s)	1508(m)	1456	52	1433(m)	425	501
[Ni(Quin) ₂ (α -Pic) ₂].2H ₂ O	1562(s)	1510(m)	1465	45	1404(s)	468	494
[Cu(Quin) ₂ (α -Pic) ₂].2H ₂ O	1462(s)	1568(s)	1375	193	1437(m)	420	468
[Zn(Quin) ₂ (α -Pic) ₂].2H ₂ O	1464(s)	1610(s)	1377	233	1438(m)	412	443
[Cd(Quin) ₂ (α -Pic) ₂].2H ₂ O	1561(m)	1507(m)	1464	43	1432(m)	410	442
[Hg(Quin) ₂ (α -Pic) ₂]	1608(s)	1560(m)	1460	100	1430(m)	425	445

Where: s = strong, m = medium

Table-3: Electronic spectra data of the ligands (QuinH), (α -Pic) and their metal complexes in DMSO solvent

Compound	λ_{\max} nm	Wave number cm^{-1}	ϵ_{\max} Molar $^{-1}\text{cm}^{-1}$	Assignment
[QuinH] [Ligand]	227	44052	1322	$n \longrightarrow \pi^*$
α -Picoline	206	48542	636	$n \longrightarrow \pi^*$
[Mn(Quin) $_2$ (α -Pic) $_2$] .2H $_2$ O	292 311	34246 32154	1612 1489	C.T ${}^6A_{1g} \longrightarrow {}^4T_{2g}(D)$
[Co(Quin) $_2$ (α -Pic) $_2$]	299 324 630 876	33444 30864 15873 11415	1001 58 30 25	C.T ${}^4T_{1g} \longrightarrow {}^4T_1(P) {}^4T_{1g}$ $\longrightarrow {}^4A_{2g} {}^4T_{1g}$ $\longrightarrow {}^2T_{2g}$
[Ni(Quin) $_2$ (α -Pic) $_2$] .2H $_2$ O	303 313 640 880	33333 31948 15625 11363	1634 638 250 30	C.T ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ ${}^3A_{2g} \longrightarrow {}^3T_{1g}$
[Cu(Quin) $_2$ (α -Pic) $_2$] .2H $_2$ O	315 884	31746 11312	1357 0.020	C.T ${}^2E_g \longrightarrow {}^2T_{2g}$
[Zn(Quin) $_2$ (α -Pic) $_2$] .2H $_2$ O	303 314	33003 31847	1296 1311	C.T C.T
[Cd(Quin) $_2$ (α -Pic) $_2$] .2H $_2$ O	301 313	33222 31948	868 905	C.T C.T
[Hg(Quin) $_2$ (α -Pic) $_2$]	260 314	38461 31847	1870 1876	C.T C.T

Table-4: Nomenclature of prepared complexes

NO.	Complexes	Nomenclature
1	[Mn(Quin) $_2$ (α -Pic) $_2$].2H $_2$ O	Bis(quinaldato)bis(α -picoline)manganese(II) dihydrate
2	[Co(Quin) $_2$ (α -Pic) $_2$]	Bis(quinaldato)bis(α -picoline)cobalte(II)
3	[Ni(Quin) $_2$ (α -Pic) $_2$].2H $_2$ O	Bis(quinaldato)bis(α -picoline)nikel(II) dihydrate
4	[Cu(Quin) $_2$ (α -Pic) $_2$].2H $_2$ O	Bis(quinaldato)bis(α -picoline)copper(II) dihydrate
5	[Zn(Quin) $_2$ (α -Pic) $_2$].2H $_2$ O	Bis(quinaldato)bis(α -picoline)zinc(II) dihydrate
6	[Cd(Quin) $_2$ (α -Pic) $_2$].2H $_2$ O	Bis(quinaldato)bis(α -picoline)cadmium(II) dihydrate
7	[Hg(Quin) $_2$ (α -Pic) $_2$]	Bis(quinaldato)bis(α -picoline)mercury(II)

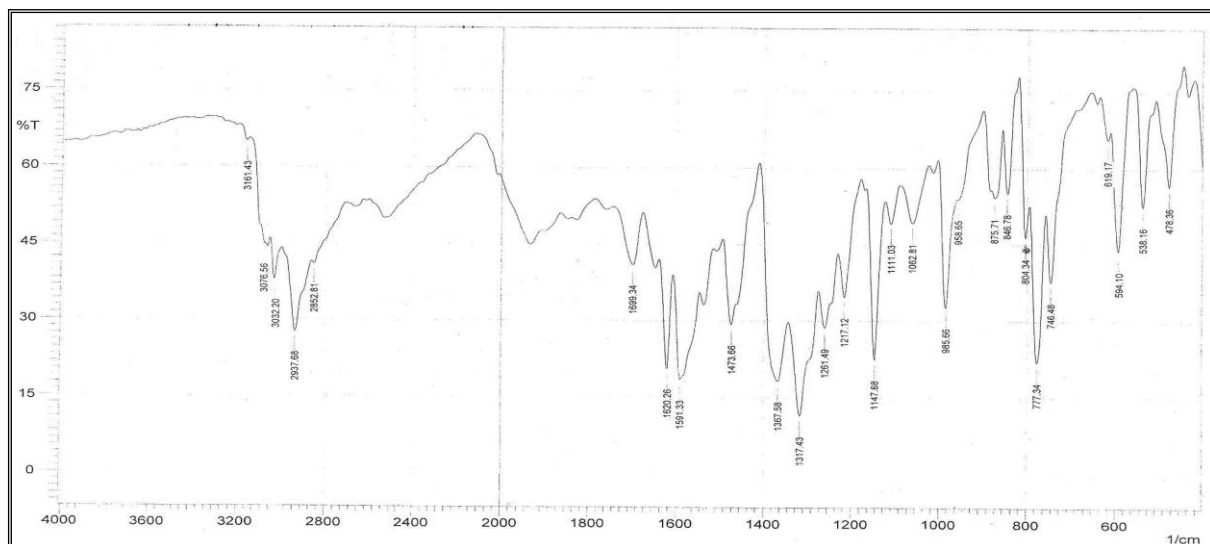


Figure-1: FT-IR spectrum of [QuinH] (L)

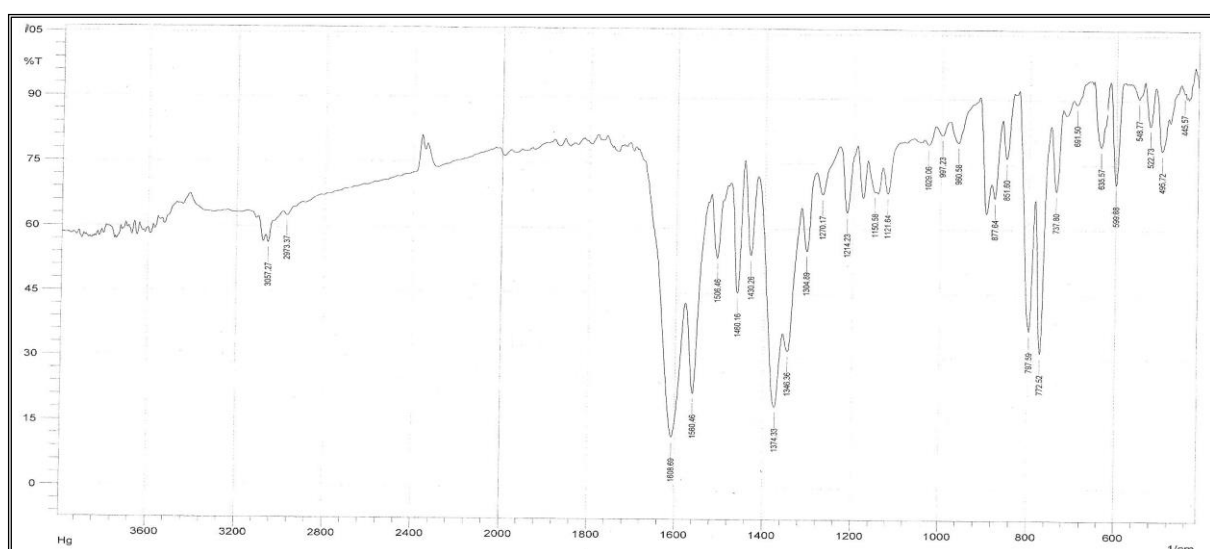
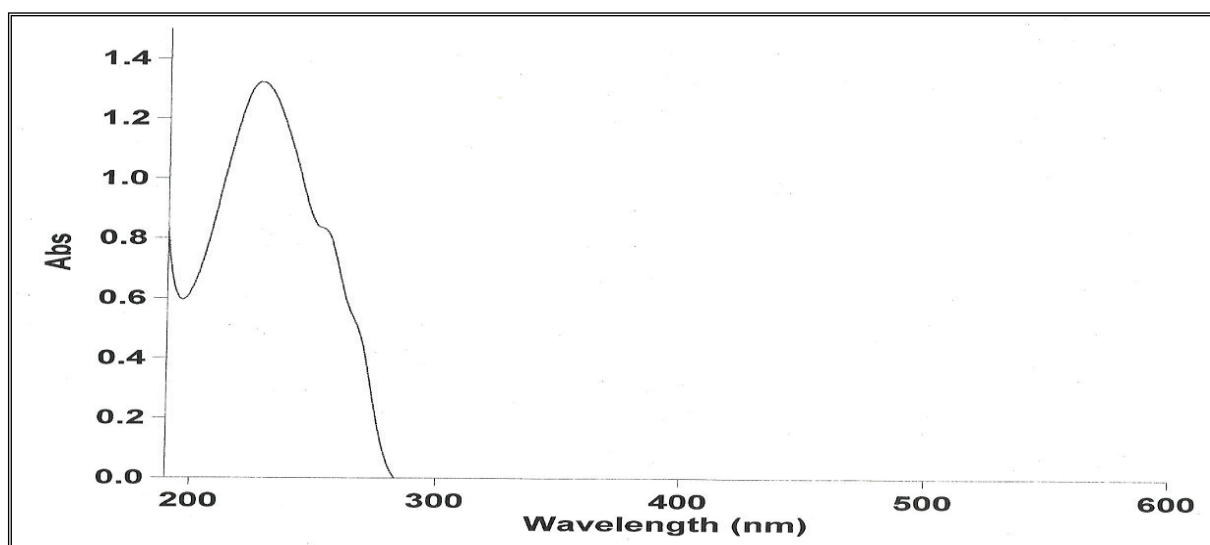
Figure-2: FT-IR spectrum of [Hg(Quin)₂(α -Pic)₂]

Figure-3: Electronic spectrum of [QuinH] (L)

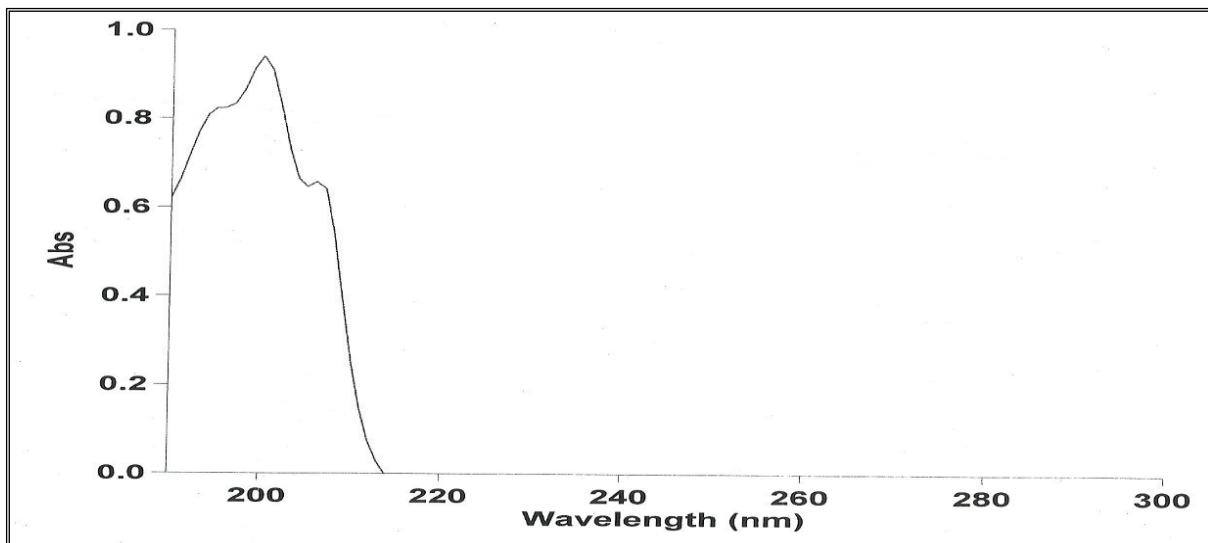


Figure-4: Electronic spectrum of α -Picoline

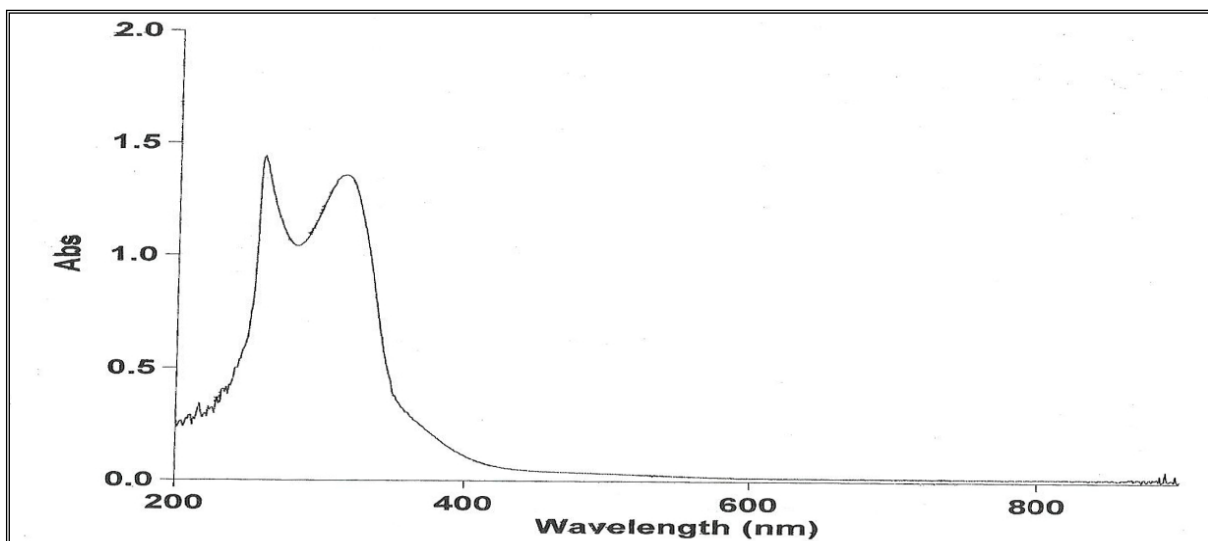


Figure-5: Electronic spectrum of $[\text{Cu}(\text{Quin})_2(\alpha\text{-Pic})_2] \cdot 2\text{H}_2\text{O}$

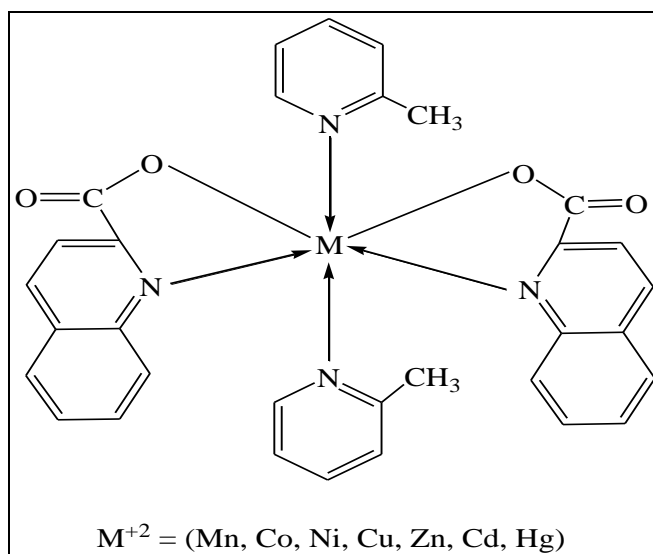


Figure-6: General structure of complexes

CONCLUSIONS

Some metal ions (Mn^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} and Hg^{+2}) complexes of quinaldic acid and α -picoline have been synthesized and characterized on the basis of their (FT-IR, UV-Vis) spectroscopy. The complexes showed octahedral geometry around the metal.

REFERENCES

1. E. E. Ebenso, I. B. Obor and L. C. Murulana, "Quinoline and derivatives as effective corrosion inhibitors for mild steel in acidic medium" *Int. J. Electrochem. Sci.*, Vol. 5, 1574 (2010).
2. C.-H. Lee and H.-S. Lee, "Growth inhibiting activity of quinaldic acid isolated from ephedra pachyclada against intestinal bacteria" *J. Korean Soc. Appl. Biol. Chem.*, Vol. 52, No. 4, 331 (2009).
3. W. Li, M. M. Olmstead, D. Miggins and R. H. Fish, "Synthesis and structural studies of metal complexes of biological ligand 2-quinaldic acid: Utilization of the polymer pendant analog PS-2-QA for selective aluminum ion removal from aqueous solution" *Inorg. Chem.*, Vol. 35, 51 (1996).
4. D. T. Houghton, N. W. Gydesen, N. Arulsamy and M. P. Mehn, "Synthesis and characterization of iron(II) quinaldate complexes" *Inorg. Chem.*, Vol. 49, 879 (2010).
5. A. D. Chowdhury, A. Das, K. Irshad, S. M. Mobin and G. K. Lahiri, "Isomeric complexes of $[Ru^{II}(trpy)(L) Cl]$, ($trpy = 2,2':6',2''$ -terpyridine and $HL =$ quinaldic acid): Preference of isomeric structural from in catalytic chemoselective epoxidation process" *Inorg. Chem.*, Vol. 50, No. 5, 1775 (2011).
6. E. Lodyga-Chruscinska, G. Micera and E. Garribba, "Complex formation in aqueous solution and in the solid state of the potent insulin-enhancing ($V^{VI}O^{2+}$) compounds formed by picolinate and quinolinate derivatives" *Inorg. Chem.*, Vol. 50, 883 (2011).
7. Ban Z. Neema, M.Sc. Thesis "Synthesis and studied of mixed-ligand complexes of N-acetyl DL-tryptophan and amine adducts with some metal salts" University of Baghdad (2008).
8. R. M. Silverstein, G. C. Bassler and T. C. Morrill, "Spectrometric Identification of Organic Compound", 4th Ed., 1981, John Wiley and Sons, Inc., New York.
9. R. J. Dyer "Application of Absorption Spectroscopy of Organic Compounds" Prentice-Hall, Inc., 1965, Englewood Cliffs, N. J., London.
10. Y. R. Sharma, "Organic Spectroscopy Principles and Chemical Applications" S. CHAND & company LTD. 2000, Canisogool.
11. K. Nakamoto "Infrared Spectra of Inorganic and Coordination Compound", 4th Ed., 1996, John Wiley and Sons, New York.

12. G. M. Trigiano, L. Menabue and G. C. Pellaani, "Exchange interactions synthesis, spectroscopic and magnetic properties of mixed-ligand complexes of copper(II) with imidazole and nitrogen-protected amino acid", *J. Inorg. Nucl. Chem.*, Vol. 47, No. 11, 2431 (1975).
13. K. Nakamoto and J. Kieft, "Infrared spectra of some platinum(II) glycine complexes" *J. Inorg. Nucl. Chem.*, Vol. 29, 2561 (1967).
14. N. N. Greenwood and K. Wade, "Spectral and electrochemical study of coordination molecules $\text{Cu}_4\text{OX}_6\text{L}_4$, 3-methyl pyridine and 4-methyl pyridine $\text{Cu}_4\text{OBr}_n\text{Cl}_{(6-n)}\text{L}_4$ complexes" *J. Chem. Soc.*, Vol. 4, 1130 (1960).
15. D. Nichllis, "Complexes and first-row transition elements" *Macmilolan Chem. Text*, Vol. 6, No. 4, 73 (1979).
16. L. F. Heidt, G. F. Koster and A. M. Johnson, "Absorption spectrum of manganese(II) diethylene triamine complexes" *J. Am. Chem. Soc.*, No. 80, 6471 (1958).
17. C. K. Jorgensen, "Synthesis, characterization and antibacterial activity of Mn(II), Co(II), Ni(II) and Cu(II) complexes of 4-carboxaldehyde phenyl hydrozone-1-phenyl-3-methyl-2-pyrazoline-5-one" *Chem. Phys.*, No. 5, 33 (1963).
18. S. M. Al-Hashimi, B. M. Sarhan and A. Y. Alwan, "Synthesis and characterization of mixed-ligand complexes containing N-acetyl glycine and pyridine with some metal ions" *Ibn-Al-Haitham J. for Pure and Apli. Sci.*, No. 4, 8 (2005).
19. P. Battaglia, A. B. Corradi, G. Maracortrigilano, L. Menabue and G. C. Pellacuni, "Synthesis and spectroscopic and structural properties of bis(N-acetyl DL-tryptophane copper(II) complex and its amine adducts effect of amines on the amine acid coordination" *J. Am. Chem. Soc.*, Vol. 102, No. 8, 2663 (1980).
20. D. Sutton, "Electronic Spectra of Transition Metal Complexes", 1968, McGraw-Hill, New York,.
21. A. B. Lever, "Coordination Chem. Rer." No. 3, 119 (1968).
22. J. F. Huheey, "Inorganic Chemistry, Principles of Structure and Reactivity" 3rd Ed., 1983, Harper International SI Edition: Maryland.