Synthesis and study of some mixed ligand complexes of Caffeine , γ-picoline and Thiocyanate with some metal ions

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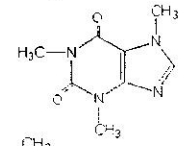
Abstract:

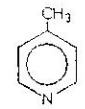
This paper presents the preparation and study of some mixed ligand complexes of caffeine, γ-picoline and thiocyanete ions with some metal ions. The reaction was carried out in (1:1) ethanol: water mixture using the appropriate molar ratio of metal: ligand (1:1:1:2) as required. The resulting products were found to be solid crystalline complexes which have been characterized by using I.R, U.V-Visible spectra, elemental analysis, thermal stability, molar conductivity and magnetic properties. The general formula of the prepared complexes given $[M(CA)(\gamma\text{-pico})X_2]$ was suggested as.

Where $M^{2+} = VO^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$

CA= Caffeine ($C_8H_{10}O_2N_4$)



γ-pico= γ-picoline (C_6H_7N)



X^-= Thiocyanate ion (SCN^-).

Introduction:

Caffeine (1,3,7-trimethyl xanthine) is found in coffee, tea, cola nuts, Coca Cola, and Cocoa. Caffeine is stimulant of central nervous system, cardiac muscle and respiratory system. Diuretic delays, fatigue. New study finds that caffeine may prevent skin cancer at least in mice[1].

Some caffeine complexes were found bioloyically active. The complex $[P(C_6H_5)_3(CH_3)][PtCl_3$ (Caffeine)] is anticancer[2]agent. Zinc carboxylate complexes with caffeine $(CH_3CH_2COO)_2$ Zn (Caffeine). H_2O have potential antifungal effect[3]. The other caffeine complexes like $[Mg(SCN)_2(caffeine)_2.7H_2O]$[4], [Cu(Clofibriate)$_2$.caffeine][5], [Cu(Pyridine-2,6-dicarboxylate) caffeine][6] have antimicrobial effect.

Materials and instrumentation:

The chemical used in this work were all pure grade ($VOSO_4.H_2O$, $CoCl_2$. $6H_2O$, $NiCl_2$. $6H_2O$, $CuCl_2$. $2H_2O$, $ZnCl_2$, $Cd(No_3)_2$. $4H_2O$, KSCN, KBr) from Riedeldehaenag, [γ.picoline, caffeine] from May and Baker Ltd., and Dimethyl Sulfoxide and ethanol from Fluka.

The I.R spectra in the region $(4000\text{-}400)cm^{-1}$ were recorded by using Shimadzu. FTIR. 8400S Fourier transform infrared spectrophotometer, the U.V-Visible spectra were recorded by Shimadzu U.V-Visible recorder spectrophotometer U.V-160. in DMSO solution $(10^{-3})M$ and the conductivity measurement were carried out at capacitor analyzer and resistance bridge type CRB_3 in DMSO solution $(10^{-3})M$ at room temperature. all this measurements recorded in College of

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Science /Baghdad University.

The elemental analysis of the complexes were recorded by Perkin Elemer B. 240 elemental analyzer in College of Science/ Al-Mousel University.

The Balance magnetic susceptibility model MSB-MKI was used to measure the magnetic susceptibility in College of Science/ Al-Nahrayian University. Finally the melting points were recorded by Stuart melting point apparatus.

General procedure for the synthesis of the complexes using the appropriate amounts of the chemicals according to the decided molar ratio (1:1:1:2) (M:CA: γ-Pico: X), an ethanolic solution of caffeine was added to an aqueous solution of metal salts followed by the addition of γ-picoline and the aqueous solution of potassium thiocyanate.

Successively, the mixture was continuously stirred at room temputure, immediate precipitates were obtained, the products were filtered off, washed with ethanol, recrystallization from ethanol and dried at 60°C.

Results and Discussion:-

Solubility:-

All the complexes prepared in this work were insoluble in water, methanol, and acetone but soluble in dimethylformamide,and dimethylsulfoxide.

Thermal stability:-

All the complexes are thermally stable as they decompose above 300°C (cadmium complexes decomposed at 298°C).

Molar conductance:-

Molar conductance values were found in the range (4.470-15.2)ohm^{-1}.cm^2.mol^{-1}. which indicates that the complexes are non-electrolytes[7,8]. These were determined in (DMSO) solution (10^{-3}M).

Physical properties and elemental analysis are listed in table (1).

Magnetic Properties:-

The magnetic moment (μ_{eff}) for the complexes of (VO^{2+} and Cu^{2+}) d^1 were found to be (1.540)B.M, (1.872)B.M respectively., within the expected value for one electrone.

The (μ_{eff}) value for the following high spin tetrahedral complexes were found as follows: for Co^{2+} (d^7) complexes is (3.761) B.M within the expected spin-only values[9,10].

The higher value of (μ_{eff}) for Ni^{2+} (d^8) complexes (3.366) B.M may be due to orbital contribution[9,11].

The complexes of Zn^{2+}, Cd^{2+} are diamagnetic as expected from their electron configuration. All data and remarks are found in table (2).

The Electronic Spectra:-

Electronic Spectra of free ligands:-

The electronic spectra data (table 3) in DMSO show strong absorption band of caffeine at λ_{max} (275) n.m (36363.636)cm^{-1} attributed to $\pi\rightarrow\pi^*$, another bands at λ_{max} (316, 365)n.m (31645.569, 27397.26) cm^{-1} respectively assigned to $n\rightarrow\pi^*$.

The gamma picoline spectra show absorption bands at λ_{max} (232, 289) n.m (43103.448, 34602.076) cm^{-1} respectively due to ($\pi\rightarrow\pi^*$), and the another bands are due to ($n\rightarrow\pi^*$) potassium thiocyanate spectra exhibited absorption band at λ_{max} (235) n.m (42553.191)cm^{-1} and λ_{max} (266) n.m (37593.985) cm^{-1} are due to ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) respectively.

The Electronic spectra of the complexes:-

1. [VO(CA)(γ.pico)X_2]

The spectrum of the green vanadyl complex exhibited absorption band at λ_{max} (280)nm (25714.285)cm^{-1} attributed to charge transfer, and the band at λ_{max} (907)nm (11025.358)cm^{-1}

attributed to the electronic transition (d-d). Selbin and Jorgensen suggested the square pyramid for the five coordination $[VO(acac)_2]$ and for $[VO(oxalato)_2]$[12,13] accordingly the probable structure to $[VO(CA)(\gamma.pico)X_2]$ is square pyramid.

2. $[Co(CA)(\gamma.pico)X_2]$

The spectrum of the pink complex showed an absorption band at λ_{max} (265)nm (37735.849)cm^{-1} attributed to shift of ligand band to higher wave charge transfer, band at another band appeared at (426,532)nm (23474.178, 18796.992)cm^{-1} was attributed to $^4A_{2(F)} \rightarrow {}^4T_{1(F)}$ transition. A third band appeared at λ_{max} (805, 983)nm (12422.36, 10172.94)cm^{-1} was assigned to $^4A_{2(F)} \rightarrow {}^4T_{2(F)}$ electronic transition.

These values are accepted for cobalt (II) tetrahedral complexes[14].

3. $[Ni(CA)(\gamma\text{-pico})X_2]$

The spectrum of the green-blue complex of Ni(II) showed absorption bands at λ_{max} (269)nm (37174.721)cm^{-1}, indicate a shift of legand band to higher frequencies. Bands appeared at λ_{max} (405)nm (24691.358)cm^{-1} and λ_{max} (990)nm (10101.01)cm^{-1} were attributed to the electronic transitions $^3T_{1(F)} \rightarrow {}^3A_{2(F)}$, $^3T_{1(F)} \rightarrow {}^3T_{1(P)}$ and $^3T_{1(F)} \rightarrow {}^3T_{2(F)}$ respectively these transition are characteristic for tetrahedral complexes of Ni(II)[14].

4. $[Cu(CA)(\gamma\text{-pico})X_2]$

The gray complex of Cu(II) exhibited bands in the visible region at λ_{max} (536, 781)nm (18656.716, 12804.097)cm^{-1} belong to electronic transition $^3T_{2(D)} \rightarrow {}^2E_{(D)}$.

The complexes $[Zn(CA)(\gamma\text{-pico})X_2]$ and $[Cd(CA)(\gamma\text{-pico})X_2]$: The electronic configuration of Zn(II) and Cd(II) is (d^{10}) which confirm absence of any (d-d) transitions[12-16], but the absorption bands in their spectra suffered blue shift with Hypo or Hyper chronic effect. All the data and remarks are included in table (3).

Infrared spectra:

Infrared spectra of free ligands:

The spectrum of caffeine showed weak and sharp band at (3111)cm^{-1} belong to stretching vibration ν(C-H) aromatic[17-19]. Another weak band belong to str. vibr ν(C-H) aliphatic was found at (2952.8)cm^{-1} [17], the strong broad band at (1720)cm^{-1} attributed to str.vibr of ν(C=O), strong and broad band at (1658.7)cm^{-1} attributed to the str.vibr. ν(-N=C<) [20]. Finally the str.vibr. ν(C=C) was noticed at (1546.8)cm^{-1} with shoulder at (1600.8)cm^{-1} [21].

In the spectrum of γ-picoline two bands were noticed at (3050)cm^{-1} and (2950)cm^{-1} attributed to str.vibr. of ν(C-H) aromatic and aliphatic respectively. and the band at (1645)cm^{-1} was assigned as str.vib. ν(-N=C<) wheres the ν(C=C) was found at (1550)cm^{-1}.

The potassium thiocyanate spectrum appeared very strong band at (2048.3)cm^{-1} caused by the str.vib. ν(-C=N)[22-25], the band at (740.6)cm^{-1} assigned as str.vib. ν(=C=S)[22].

Infrared spectra of complexes:

The infrared spectra of the prepared complexes as KBr disc exhibited str.vib. ν(C-H) aromatic in the region (3031.89-3049.25)cm^{-1}, bands in the range (1614.31-1635)cm^{-1} belong to the ν(-N=C<) show shift to lower frequencies by (44.39-23.7)cm^{-1} in comparison with caffeine and by (30.69-10)cm^{-1} in comparison with gamma picoline spectra which indicated the coordination of the ligands with the metal ions through the nitrogen atoms in their structures.

The $(SCN)^-$ group may coordinate to metal through the nitrogen or the sulfur atoms[26]. The complexes prepared in this paper show linkage isomerism as the S-bonded

Table (1) The physical properties of the metal complexes [M(CA)(γ-pico)X_2]

No.	Compound	Colour	M.P.C°	Dec°.	Elemental analysis: Calc (Found)%			%M Calc (found)	Molar conductivity Λ(ohm^{-1}.Cm^2.mol^{-1} 10^{-3}M in DMSO
					%C	%H	%N		
1	Caffeine (CA) ($C_8H_{10}O_2N_4$)	White	234	> 300	-	-	-	-	12.5
2	γ-Picoline (γ-pico) (C_6H_7N)	Yellow	145 B.P.C°	-	-	-	-	-	7.307
3	KSCN	White	173	> 300	-	-	-	-	27.27
4	[VO(CA)(γ-pico)X_2] ($C_{16}H_{17}O_2N_7S_2$)VO	Dark green	-	> 300	40.851 (40.63)	3.639 (2.81)	20.841 (20.70)	10.828 (11.228)	15.2
5	[Co(CA)(γ-pico)X_2] ($C_{16}H_{17}O_2N_7S_2$)Co	Pink	192	> 300	41.559 (41.33)	3.702 (3.51)	21.202 (21.10)	12.744 (11.585)	5.428
6	[Ni(CA)(γ-pico)X_2] ($C_{16}H_{17}O_2N_7S_2$)Ni	Green-blue	-	> 300	41.579 (40.46)	3.703 (3.65)	21.212 (21.15)	12.702 (12.191)	5.629
7	[Cu(CA)(γ-pico)X_2] ($C_{16}H_{17}O_2N_7S_2$)Cu	Gray	-	> 300	41.149 (41.11)	3.665 (3.54)	20.993 (19.87)	13.605 (12.173)	4.470
8	[Zn(CA)(γ-pico)X_2] ($C_{16}H_{17}O_2N_7S_2$)Zn	White	142	> 300	40.987 (41.77)	3.651 (2.43)	20.910 (19.83)	13.927 (12.672)	4.75
9	[Cd(CA)(γ-pico)X_2] ($C_{16}H_{17}O_2N_7S_2$)Cd	White	204	298	37.251 (36.19)	3.318 (2.26)	19.004 (19.50)	21.787 (21.548)	5.066

Table (2) The magnetic properties of the complexes at (25)C°

No	Complexes	No. of electrons	Electron configuration	Term symbol	Term symbol in ground state in Td	Orbital contribution	μ_{eff}	
							Found	Calc.
1	[VO(CA)(γ-pico)X_2]	d^1	t_2g^1	-	-	-	1.540	1.732
2	[Co(CA)(γ-pico)X_2]	d^7	$e^4t_2^3$	^4F	$^4A_2$	No	3.761	3.872
3	[Ni(CA)(γ-pico)X_2]	d^8	$e^4t_2^4$	^3F	$^3T_1$	Yes	3.366	2.828
4	[Cu(CA)(γ-pico)X_2]	d^9	$e^4t_2^5$	^2D	$^2T_2$	Yes	1.872	1.732
5	[Zn(CA)(γ-pico)X_2]	d^{10}	$e^4t_2^6$	^1S	-	-	Zero	Zero
6	[Cd(CA)(γ-pico)X_2]	d^{10}	$e^4t_2^6$	^1S	-	-	Zero	zero

Table (3) U.V-visible spectra of free ligands and their complexes $(10)^{-3}$M in DMSO

No	Compounds	λ_{max} n.m	ABS	Wave number (Cm^{-1})	ε_{max} ($L.mol^{-1}.cm^{-1}$)	Transitions	Remarks
1	CA	275	1.774	36363.636	1774	π→π*	-
		316	0.006	31645.569	6	n→π*	-
		365	0.014	27397.26	14	n→π*	-
2	γ-pico	232	0.145	43103.448	145	π→π*	-
		289	2.182	34602.076	2182	π→π*	-
		350	0.500	28571.428	500	n→π*	-
3	KSCN	235	0.108	42553.191	108	π→π*	-
		266	0.529	37593.985	529	n→π*	-
4	[VO(CA)(γ-pico)X_2]	280	2.167	35714.285	2167	Charge transfere (C.T)	-
		907	0.025	11025.358	25	d-d	New band

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5	[Zn(CA)(γ-pico)X_2]	d^{10}	$e^4t_2^6$	^1S	-	-	Zero	Zero
6	[Cd(CA)(γ-pico)X_2]	d^{10}	$e^4t_2^6$	^1S	-	-	Zero	zero

Table (3) U.V-visible spectra of free ligands and their complexes $(10)^{-3}$M in DMSO

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5	[Co(CA)(γ-pico)X_2]	265	1.075	37735.849	1075	$^4A_{2(F)} \rightarrow {}^4T_{1(P)}$ (ν_3)	(C.T)
		426	0.005	23474.178	5	$^4A_{2(F)} \rightarrow {}^4T_{1(F)}$ (ν_2)	-
		532	0.018	18796.992	18		
		805	0.001	12422.36	1	$^4A_{2(F)} \rightarrow {}^4T_{2(F)}$ (ν_1)	-
		983	0.009	10172.94	9		
6	[Ni(CA)(γ-pico)X_2]	269	1.583	37174.721	1583	$^3T_{1(F)} \rightarrow {}^3A_{2(F)}$ (ν_2)	(C.T)
		347	0.011	28818.443	11	-	-
		405	0.024	24691.358	24	$^3T_{1(F)} \rightarrow {}^3T_{1(P)}$ (ν_3)	-
		990	0.017	10101.01	17	$^3T_{1(F)} \rightarrow {}^3T_{2(F)}$ (ν_1)	-
7	[Cu(CA)(γ-pico)X_2]	291	1.011	34364.261	1011	(C.T)	-
		536	0.003	18656.716	3	$^2T_{2(D)} \rightarrow {}^2E_{(D)}$	-
		781	0.016	12804.097	16		
8	[Zn(CA)(γ-pico)X_2]	276	1.962	36231.884	1962	(C.T) (M→L)	-
9	[Cd(CA)(γ-pico)X_2]	270	1.053	37037.037	1053	(C.T) (M→L)	-
		343	0.002	29154.519	2	-	-

Table (4) The characteristic bands of infrared spectra of the ligands and their complexes

No	Compound	ν (C-H) aromatic	ν(C-H) aliphatic	ν (CN) (-SCN)	ν (CN) (-NCS)	ν(C=O)	ν(-N=C())	ν(C=C)	ν (CS) (-NCS)	ν (CS) (-SCN)	ν(M-N)	δ (M-SCS)	δ(M-SCN)
1	Caffeine (CA)	3111 w.sh	2952.8 w. sh asy. 2891.1 w	-	-	1720 s.b	1658.7 s.b	1698.8 sho 1546.8 S	-	-	-	-	-
2	γ-Picoline (γ-pico)	3050 w. sh	2950 sho	-	-	-	1645 s.sh	1550 sho	-	-	-	-	-
3	[VO(CA)(γ-pico)X_2]	3035.75 v.w	2954.74 v.w	2152.41 2140.84 w.b	2081.05 2065.62 w.b	1701.80 m.sh	1635 s.sh	1541.02 m.sh	761.83 w.sh	744.17 m.sh	526.53 v.w 513.03 v.w	482.17 w. sh	443.60 v.w 426.24 v.w
4	[Co(CA)(γ-pico)X_2]	3041.53 v.w	2939.31 v.w	2115.77 vs.sh	2067.55 sho	1700 v.w	1616.24 s.sh	1560.30 w.sh	810.05 s.sh	730 w.sh	541.96 w	489.89 s.sh	415 w.sh
5	[Ni(CA)(γ-pico)X_2]	3035.75 v.w	2958.60 v.w	2111.91 v.s	2050 sho	1701.10 v.w	1648.17 m.sh	1544.88 v.w	808.12 s.sh	730 v.w	535 v.w	497.60 s.sh	450 v.w
6	[Cu(CA)(γ-pico)X_2]	3037.68 v.w	2956.67 v.w	2140.13 v.s	2088.76 v.s	1701.10 v.w	1618.17 w.sh	1540 v.w	800 w. sh	740 w.sh	550 v.w	500 w.sh	430 sho
7	[Zn(CA)(γ-pico)X_2]	3031.89 v.w	2947.03 v.w	2090.69 v.s	2042.48 sho	1701.10 m	1629.74 m.sh	1548.73 w	808.12 s.sh	740 w.sh	550 w.sh	489.89 s.sh 478.31 sho	430 v.w
8	[Cd(CA)(γ-pico)X_2]	3049.25 v.w	2927.74 v.w	2104.19 v.s	3092.62 sho	1701.10 v.w	1614.31 s.sh	1560.30 w.sh	804.26 s.sh 771.40 w.sh	723.26 w.sh	536.17 m.sh	489.89 vs.sh 460.96 w.sh	440 sho

S= strong, m=medium, w=weak, b=broad, sh= sharp, Sho=shoulder, V= very, Sy= symmetry, asy= asymmetry.

ν(-SCN) was shifted to higher frequencies by (42.39-111.83)cm^{-1} whereas ν(CN) in N-bonded (-NCS) was moved by (5.82-44.32)cm^{-1} to higher frequency. Similar absorption have been found in the I.R spectra of [Pd(4,4`-dimethyl bipyridine)(NCS)(SCN)][27], [Pd{$Ph_2P(CH_2)_3NMe_2$}{(NCS)(SCN)}][28], [$Pb(AsPh_3)_2$(NCS)(SCN)][26,29-31].

M-ligand bonds:

The coordination of ligands to metal ions was further confirmed by the weak bands between (513.03-550)cm^{-1} indicating the ν(M-N) bond. The bands in the region (460.96-500)cm^{-1} and (426.24-450)cm^{-1} were assigned to δ(M-NCS) and δ(M-SCN) respectively. All data are in table (4).

Suggested Geometries:

From all above characteristic studies the following geometrical shapes could be suggested:-

a. Squar pyramid for [VO(CA)(γ-pico)(SCN)(NCS)].
b. Tetrahedral for [M(CA)(γ-pico)(SCN)(NCS)] where M=Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}.

CA= Caffeine

γ-pico= gamma- picoline.

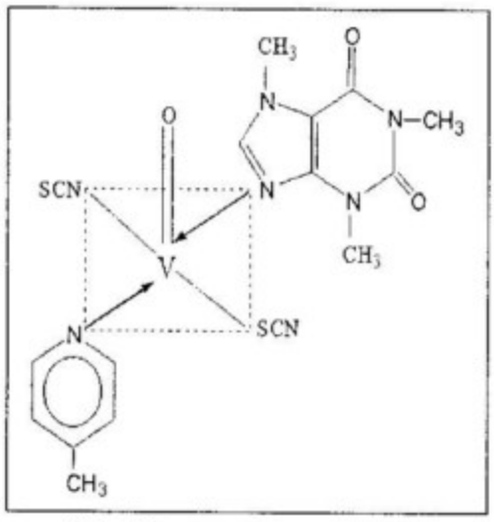

Fig (1)

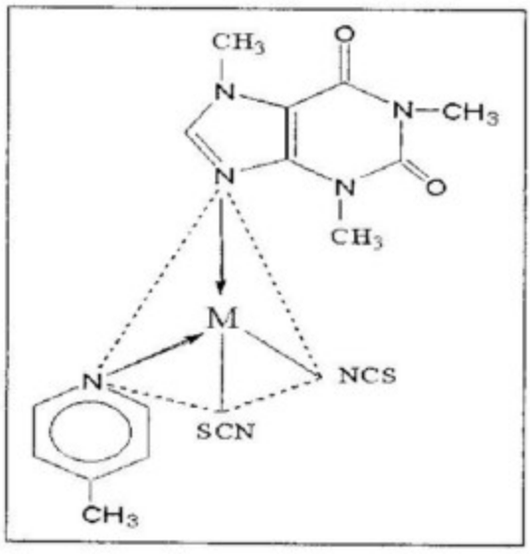

Fig (2)

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تخليق ودراسة معقدات ذات لكاندات مختلطة من الكافائين وكاما بيكولين وأيون الثايوسيانات مع بعض الايونات الفلزية.

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الخلاصة:

لقد تم في هذا البحث تحضير وتشخيص معقدات ذات لكاندات مختلطة من الكافائين والبيكولين وأيون الثايوسيانات مع بعض الايونات الفلزية وقد تمت المفاعلة في مذيب الايثانول والماء المقطر بنسبة (١: ١) وبالنسبة المولية (١: ١: ١: ٢) والمعقدات المحضرة عبارة عن مواد صلبة بلورية بعضها ملون وقد تمت دراسة هذه المعقدات بالطرق الاتية:- التوصيلية المولارية، تحليل العناصر (الكربون، الهيدروجين، النتروجين) بالاضافة الى حسابات النسبة المئوية للفلز في المعقد وقياس الخاصية المغناطيسية. كما تمت دراستها طيفيا باستخدام (الاشعة فوق البنفسجية- المرئية والاشعة تحت الحمراء) وعلى اساس هذه الدراسات تبين ان كلاً من الكافائين والكامابيكولين سلكا كلكاندين احاديي السن تناسقا مع الايونات الفلزية عن طريق ذرة النتروجين اما ايونا (SCN) احداهما تناسقت عن طريق ذرة الكبريت والاخرى عن طريق ذرة النتروجين وبناءً على ماتم استنتاجه فقد اعطيت لهذه المعقدات الصيغة العامة $[M(CA)(\gamma\text{-pico})X_2]$ اذ ان

$Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, VO^{2+} = M^{2+}$

Caffeine = CA

γ-picoline=γ-pico

X^- =ايون الثايوسيانات.