Synthesis and Studies of Mixed-Ligand Complexes of Some Transition Elements

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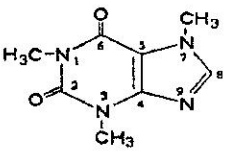
Abstract:-

This work presents the synthesis and identification of some mixed, ligand complexes with some transition elementals. These complexes containing from two to four different ligands. No report have been found on this work according to the internet informations up to 2003. The prepared complexes were characterized on the bases of their elemental analyses (C, H, N), metal percentage determination, IR and UV-Vis spectroscopy, conductivity measurements as well as their magnetic moments. The complexes have been classified into five groups with the general formulae as follows.

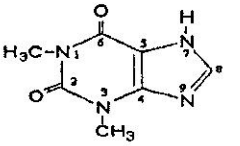
1. $[M(CA)_4Y_2]$.
2. $[M(TP)_4Y_2]$.
3. $[M(CA)_2(Ad)X_2]$.
4. $[M(TP)_2(Ad)X_2]$.
5. $[M(CA)_2(TP)_2XY]$.

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

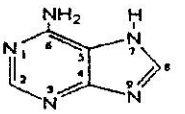
CA = Caffeine



TP= Theophylline



Ad= Adenine



X= Thiocyanateion (SCN^-)
Y= Cyanate ion (OCN^-)

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Introduction:

Caffeine (1,3,7-trimethyl xanthine) is one of the purine alkaloids it belongs to the xanthine chemical groups. It has very interesting pharmacological properties which is very important from abiological point of view[1]. Caffeine probably the most popular drug in the world, we consume caffeine in coffee, tea and some soft drinks. In massive doses caffeine lethal[2]. Einar and Sletten[3] have carried out extensive synthetic work on transition metal complexes of purine derivatives they concluded that the chelating sites of copper (II) adenine complexes are probably the nitrogen atoms N(3) and N(9). The anion derived from theophylline has often be used as model ligand in studying the interaction with metal ions[4]. In this work we presented the synthesis and identification of some metal element complexes containing caffeine, theophylline and adenine as mixed ligand complexes. The prepeared complexes containing from two to four different ligands have been find to be quite stable.

Experimental:

Materials and measurements:

All chemicals were obtained from commercial sources and were used without further purifications ($VOSO_4$. H_2O, $CoCl_2.6H_2O$, $NiCl_2$. $6H_2O$, $CuCl_2$. $2H_2O$) (KSCN, KOCN) from (Riedeal –Dehaenage & Fluka). (Caffeine, adenine, theophylline) from (BDH).

The I.R. Spectra in the range (4000-400)Cm^{-1} were recorded as potassium bromid disc on shimadzu FTIR-8300 fourier transform infrared spectrophotometer. UV-Visible spectra were measured in (DMSO) using shimadzu UV-Visible recorder spectrophotometer UV-160. Elemental analysis (C.H.N) were performed by the micro analytical unit on berkin-Elemer B-240 Elemental Analyzer in chemistry department. College of Science, University of Mousel. Determination of metals were carried out using Laboratory methods. Conductivity measurements were carried out at (25)C^0 in (DMSO) using Philips Pw-9526 digital conductivity meter. Melting were determined by using Stuart-Melting Point Apparatus and Finally the magnetic susceptibility measurements were obtained using Balance Magnetic Susceptibility Model MsB-MK1 in Chemistry Department College of Science University of Nahrayeen.

General Procedure for Synthesis:

Preparation of $[M(CA)_4Y_2]$: To an aqueous solution of the metal salt. (12)ml of ethanolic solution of caffeine (CA) containing (1.25-2.84)gm was added followed by addition of (5)ml aqueous solutions of KOCN (0.26-0.59)gm at (25)C^0 with constant stirring (using the approperate amounts of materials needed as decided by the molar ratio (1: 4: 2) (M: CA: Y). The resulting precipitates were filtered off. washed several time with (1: 1) water: ethanol and recrystalized from ethanol. Then dried in an oven (50-70) °C.

Similar method was followed to prepare the other complexes in groups 2, 3, 4 and 5.

Results and Discussion:

The prepared complexes of all types I, II, III, IV and V were found to be crystalline solids, insoluble in water but they are however soluble in some organic solvents like DMSO. The low value observed of molar conductivities in (DMSO) indicated the non elyctrolyte behavior of the complexes[5,6]. Elemental analyses (C.H.N) and metal determination were in good agreement with the general formulae given for all types of complexes. However the prepared complexes have been found to be relatively thermally stable since they

decomposed between (214-284)°C Table (1) gives the physical properties of the complexes.

Magnetic Susceptibility:

The magnetic moments for all complexes of vanadyl and cobalt ions should be around (1.732) B.M, and (3.872) B.M respectively while the measured values of (μ_{eff}) have been shown to be higher than the expected values, this could be related to orbital-spin coupling[7]. However the values of (μ_{eff}) of all Ni^{+2} and Cu^{+2} complexes have been found to be closer to that of spinning only[7].

All data are included in table (2).

Spectral Studies:

Electronic spectra:-

The electronic spectra for free ligands (CA, TP, Ad, OCN^- and SCN^-) show absorption bands in the UV-region expressed as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

In addition the spectra of the prepared complexes exhibited another bands in the visible region attributed to (d-d) transition which revealed ν_1, ν_2, ν_3 absorptions characteristic for complexes of octahedral geometry. This absorptions gave the following calculated ligand-field parameters i.e ligand-field splitting energy (10Dq), Racah interelectronic repulsion parameter (B), the ratio ($\beta = \frac{B^-}{B}$) which indicates the covalent nature of metal-ligand bond in the complexes, besides some absorptions suffered red shifts or blue shifts, hyper or hypo chromic effects These absorptions have been fully assigned in table (3).

Infrared Spectra:

Further informations about the coordination behavior of the free ligands with metal ions were carried out by the comparison of the infrared spectra of the free ligands and their complexes. Bands between (3320-3340) cm^{-1} attributed to ν (NH) in the structures of adenine (Ad) and theophylline (TP). These absorptions were moved to lower frequencies by (30-10)cm^{-1}.

In the spectra of the complexes containing these ligands, absorptions appeared at (1658.7)cm^{-1} and (1668.3) cm^{-1} were caused by ν (-N=C<) bond in the structures of (CA) and (TP) respectively. In the spectra of their complexes these absorptions have been lowered by (58.7-8.7) and (68.3-18.3) respectively which indicated the coordination of (CA) and (TP) to the metal ions through the nitrogen atom (N9) in their structures[1,8-10]. Similar absorptions have been found in the spectra of complexes containing adenine (Ad) ligand as the free ligand exhibited absorption at (1365.5) cm^{-1} attributed to ν (–C–N) which have been noticed in the region (1345-1360)cm^{-1} shifted to low frequencies by (20.5-5.5) cm^{-1} in the spectra of complexes which supported the coordination of (Ad) to the metal ions through the two nitrogen atoms (N3) and (N9)[11].

The asym and sym vibrations in (OCN^-) were noticed at (2165.9)cm^{-1} and (1207.4)cm^{-1} respectively in the spectra of the complexes containing this ion the asym. Str. Vib. Was found to be at higher positions in the region (2240-2260)cm^{-1}. Also the absorptions band in the case of sym. Str. Vib. was moved to higher positions in the region (1220-1250)cm^{-1} which indicated the coordination of cyanate ion through its oxygen atom[12,13]. Free (SCN^-) gave absorption band at (740.6)cm^{-1} belongs to ν(CS). This band was noticed between (640-730)cm^{-1} in the spectra of the complex. The shifting of this band to lower frequencies supported the linkage of the thiocyanate ion to the metal ion through its sulphur atom[14-17].

Ligand metal bands:

The spectra of the complexes exhibited low frequency absorptions bands in the range (560-590)cm^{-1} which have been assigned as δ(M-OCN), and another between (500-540)cm^{-1} are due to ν(M-N) while the bending. Vib δ(M-SCN) have been found (415-440)cm^{-1}.

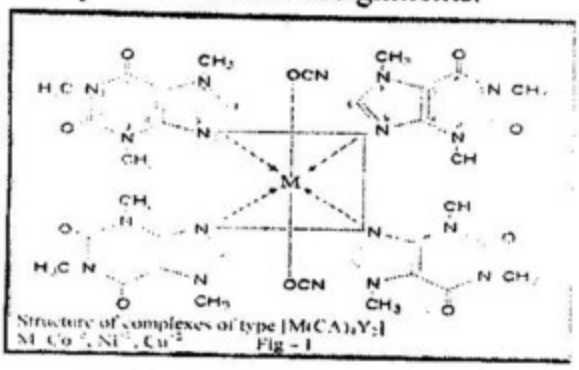
Table (4) gives the diagnostic absorptions and their assignments.

The proposed geometrical structures:

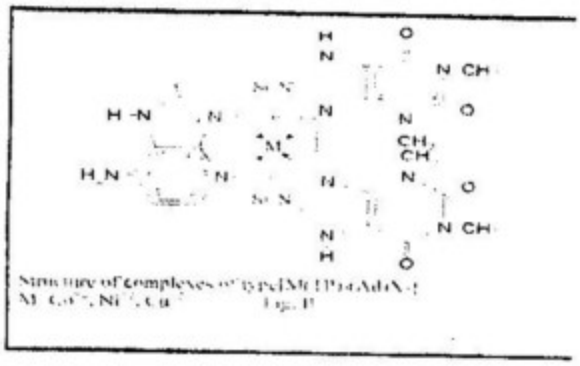
From all above studies the probable structure have been suggested:

a. Octahedral geometry for all of the complexes of Co^{+2}, Ni^{+2} and Cu^{+2}.

b. Capped octahedral for all of the vanadyl complexes.



Structure of complexes of type $[M(CA)_4Y_2]$
M: Co^{+2}, Ni^{+2}, Cu^{+2} Fig - I



Structure of complexes of type [M(TP)4AdX2]
M: Co+2, Ni+2, Cu+2 Fig. II

Table (1) The Physical properties of the free ligands and their complexes

	Compound	Colour	M.P.C°	Dec°	Elemental Analysis calc% (Found%)				Molar conductivity Λ(ohm^{-1} Cu^{2}.mol^{-1})10^{-3} M in DMSO
					%C	%H	%N	%M	
1	Caffeine CA	White	234	>300	-	-	-	-	12.5
2	KOCN	White	-	>300	-	-	-	-	26.78
3	$[VO(CA)_4Y_2]$ $(C_{24}H_{30}N_{16}O_{10})VO$	Light green	230	236	44.018 (44.12)	4.341 (4.60)	27.174 (28.10)	5.33 (5.66)	17.64
4	$[Co(CA)_4Y_2]$ $(C_{24}H_{30}N_{16}O_{10})Co$	Light Pink	238	240	44.401 (45.44)	4.379 (4.52)	27.411 (28.31)	6.33 (7)	13.04
5	$[Ni(CA)_4Y_2]$ $(C_{24}H_{30}N_{16}O_{10})Ni$	Green-yellow	256	>300	44.412 (44.29)	4.380 (4.40)	27.417 (26.51)	6.36 (6.76)	15
6	$[Cu(CA)_4Y_2]$ $(C_{24}H_{30}N_{16}O_{10})Cu$	Green-Blue	-	214	44.180 (44.22)	4.357 (5.11)	27.274 (27.30)	6.66 (7.66)	15
7	Theophylline TP	White	274	>300	-	-	-	-	13.63
8	$[VO(TP)_4Y_2]$ $(C_{28}H_{32}N_{16}O_{18})VO$	Green-Yellow	-	270	41.338 (42.43)	3.696 (2.58)	28.922 (28.70)	5.66 (6.66)	20
9	$[Co(TP)_4Y_2]$ $(C_{28}H_{32}N_{16}O_{18})Co$	Pink	260	>300	41.722 (41.65)	3.731 (3.90)	29.191 (30.25)	6.66 (7)	18.75
10	$[Ni(TP)_4Y_2]$ $(C_{28}H_{32}N_{16}O_{18})Ni$	Light Blue	-	>300	41.732 (40.83)	3.732 (3.67)	29.198 (29.27)	6.66 (7.33)	19.23
11	$[Cu(TP)_4Y_2]$ $(C_{28}H_{32}N_{16}O_{18})Cu$	Green-Blue	-	>300	41.500 (41.62)	3.711 (4.68)	29.036 (28.16)	7.3 (7.9)	15.78
12	Adenine Ad	White	-	>300	-	-	-	-	12.60
13	KSCN	White	173	>300	-	-	-	-	27.27
14	$[VO(CA)_2(Ad)X_2]$ $(C_{21}H_{21}N_{15}O_4S_2)VO$	Dark green	-	250	39.095 (39.36)	3.562 (2.75)	29.731 (29.80)	7 (7.66)	18.07
15	$[Co(CA)_2(Ad)X_2]$ $(C_{21}H_{21}N_{15}O_4S_2)Co$	Pink	250	284	39.543 (40.82)	3.603 (3.47)	30.072 (30.34)	8.33 (9.33)	17.04
16	$[Ni(CA)_2(Ad)X_2]$ $(C_{21}H_{21}N_{15}O_4S_2)Ni$	Green- Blue	-	240	39.556 (38.72)	3.604 (3.74)	30.082 (31.26)	8.33 (10)	19.73
17	$[Cu(CA)_2(Ad)X_2]$ $(C_{21}H_{21}N_{15}O_4S_2)Cu$	Gray	-	>300	39.284 (40.38)	3.580 (2.71)	29.875 (30.66)	9.03 (9.73)	23.43
18	$[VO(TP)_2(Ad)X_2]$ $(C_{21}H_{21}N_{15}O_4S_2)VO$	Dark green	-	266	37.170 (38.32)	3.116 (4.20)	30.960 (31.89)	7.5 (7.73)	18.29
19	$[Co(TP)_2(Ad)X_2]$ $(C_{21}H_{21}N_{15}O_4S_2)Co$	Pink	220	260	37.614 (38.45)	3.153 (2.23)	31.330 (31.42)	8.66 (9.66)	15.30
20	$[Ni(TP)_2(Ad)X_2]$ $(C_{21}H_{21}N_{15}O_4S_2)Ni$	Light green	254	268	37.627 (37.50)	3.154 (3.21)	31.340 (31.24)	8.73 (9.46)	16.12
21	$[Cu(TP)_2(Ad)X_2]$ $(C_{21}H_{21}N_{15}O_4S_2)Cu$	Gray	-	>300	37.358 (37.46)	3.132 (3.53)	31.116 (31.17)	9.4 (9.73)	24.19
22	$[VO(CA)_2(TP)_2XY]$ $(C_{32}H_{36}N_{18}O_4S)VO$	Dark green	-	>300	41.970 (40.87)	3.958 (4.78)	27.529 (28.61)	5.52 (6.16)	19.48
23	$[Co(CA)_2(TP)_2XY]$ $(C_{32}H_{36}N_{18}O_4S)Co$	Pink	-	>300	42.341 (42.55)	3.993 (2.73)	27.772 (27.85)	6.46 (7.56)	15.62
24	$[Ni(CA)_2(TP)_2XY]$ $(C_{32}H_{36}N_{18}O_4S)Ni$	Light green	-	>300	42.351 (42.56)	3.994 (4.84)	27.779 (28.81)	6.46 (6.76)	21.12
25	$[Cu(CA)_2(TP)_2XY]$ $(C_{32}H_{36}N_{18}O_4S)Cu$	Gray- green	-	>300	42.127 (42.14)	3.973 (3.57)	27.632 (27.79)	6.66 (7)	20.54

Table (2) The Magnetic susceptibilities for the complexes

	Complexes	d^n	Electron configuration	Term symbol	Ground state	μ_{eff} (B.M)		Orbital contribution in octahedlra.
						Found	Calc.	
1	$[VO(CA)_4Y_2]$	d^1	$t_2g^1eg^0$	^2D	$^2B_2$	1.863	1.732	Yes
2	$[VO(TP)_4Y_2]$					1.891	1.732	
3	$[VO(CA)_2(Ad)X_2]$					1.773	1.732	
4	$[VO(TP)_2(Ad)X_2]$					1.754	1.732	
5	$[VO(CA)_2(TP)_2XY]$					1.834	1.732	
6	$[Co(CA)_4Y_2]$	d^7	$t_2g^5eg^2$	^4F	^4T_1g	4.195	3.872	Yes
7	$[Co(TP)_4Y_2]$					4.037	3.872	
8	$[Co(CA)_2(Ad)X_2]$					4.090	3.872	
9	$[Co(TP)_2(Ad)X_2]$					4.188	3.872	
10	$[Co(CA)_2(TP)_2XY]$					4.258	3.872	
11	$[Ni(CA)_4Y_2]$	d^8	$t_2g^6eg^2$	^3F	^3A_2g	2.798	2.828	No
12	$[Ni(TP)_4Y_2]$					2.766	2.828	
13	$[Ni(CA)_2(Ad)X_2]$					2.898	2.828	
14	$[Ni(TP)_2(Ad)X_2]$					2.864	2.828	
15	$[Ni(CA)_2(TP)_2XY]$					2.801	2.828	
16	$[Cu(CA)_4Y_2]$	d^9	$t_2g^6eg^3$	^2D	^2Eg	1.692	1.732	No
17	$[Cu(TP)_4Y_2]$					1.678	1.732	
18	$[Cu(CA)_2(Ad)X_2]$					1.707	1.732	
19	$[Cu(TP)_2(Ad)X_2]$					1.723	1.732	
20	$[Cu(CA)_2(TP)_2XY]$					1.683	1.732	

Table (3) The electronic spectra of free ligands and their complexes

	Compound	λ_{max} n.m	ABS	Wave number (Cm^{-1})	Transitions	Remarks	lodq	B	B'	β
1	CA	275	1.774	36363.636	$\pi\rightarrow\pi^*$	-	-	-	-	-
		316	0.006	31645.569	$n\rightarrow\pi^*$	-				
		365	0.014	27397.26	$n\rightarrow\pi^*$	-				
2	KOCN	246	0.057	40650.406	$\pi\rightarrow\pi^*$	-	-	-	-	-
		272	0.614	36764.705	$n\rightarrow\pi^*$	-				
3	$[VO(CA)_4Y_2]$ REF. 18	224	0.427	44642.857	$\pi\rightarrow\pi^*$	Charge transfer(C-T) with Hyper chromic effects	-	-	-	-
		292	2.177	34246.575	$^2B_{2(t)}\rightarrow{}^2A_{1(t)}(\nu_3)$	New band with corresponding (C.T)				
		678	0.061	14749.262	$^2B_{2(t)}\rightarrow{}^2B_{2(t)}(\nu_2)$	-				
		851	0.078	11750.881	$^2B_{2(t)}\rightarrow{}^2E_{(t)}(\nu_1)$	-				
4	$[Co(CA)_4Y_2]$ REF. 19	220	0.149	45454.545	(C-T)	Blue shift with Hyper chromic effect	17285.688	971	838.371	0.863
		280	1.792	35714.285	$^4T_{1g(F)}\rightarrow{}^4A_{2g(F)}(\nu_3)$	New band with corresponding (C.T)				
		312	0.014	32051.282	-	Blue shift Hyper chromic effect				
		505	0.068	1901.98	$^4T_{1g(F)}\rightarrow{}^4T_{1g(P)}(\nu_2)$	-				
		592	0.061	16891.891						
		644	0.063	13527.95						
		767	0.042	13037.809	$^4T_{1g(F)}\rightarrow{}^4T_{2g(F)}(\nu_1)$	-				
		774	0.044	12919.896						
5	$[Ni(CA)_4Y_2]$ REF. 19	278	1.938	35971.223	(C-T)	Red shift with Hyper chromic effect	10090.817	1030	957.9	0.93
		352	0.397	28409.09	$^3A_{2g(F)}\rightarrow{}^3T_{1g(F)}(\nu_3)$	Corresponding with (C-T)				
		366	0.404	27322.404						
		991	0.014	10090.817	$^3A_{2g(F)}\rightarrow{}^3T_{2g(F)}(\nu_1)$	-				
6	$[Cu(CA)_4Y_2]$	277	1.925	36101.083	(C-T)	Red shift with Hyper chromic effect	-	-	-	-
		402	0.008	24875.621	$^2E_{g(D)}\rightarrow{}^2T_{2g(D)}$	-				
7	TP	219	0.102	45662.1	$\pi\rightarrow\pi^*$	-	-	-	-	-
		274	1.728	36496.35	$n\rightarrow\pi^*$	-				
8	$[VO(TP)_4Y_2]$	221	0.131	45248.868	$\pi\rightarrow\pi^*$	Hyperchromic effect	-	-	-	-
		279	1.841	35842.293	$^2B_{2(t)}\rightarrow{}^2A_{1(t)}$	Corresponding with (C-T) with Hyper chromic effect				
		987	0.010	10131.712	$^2B_{2(t)}\rightarrow{}^2E_{(t)}(\nu_1)$	New band				
9	$[Co(TP)_4Y_2]$	218	0.194	45871.559	(C-T)	With Hyper chromic effect	19700.55	971	351.579	0.362
		282	1.930	35460.992	$^4T_{1g(F)}\rightarrow{}^4A_{2g(F)}(\nu_3)$	New band, with corresponding (C-T)				
		585	0.132	17094.017	$^4T_{1g(F)}\rightarrow{}^4T_{2g(F)}(\nu_2)$	-				
10	$[Ni(TP)_4Y_2]$	214	0.075	46728.972		Blue shift with Hypo chromic effect	10920.493	1030	659.2	0.64

		284	1.935	35211.267	$^1A_{1g}\rightarrow{}^1T_{1g}(\nu_4)$	New band with corresponding (C-T)				
		993	0.012	10070.493	$^1A_{1g}\rightarrow{}^1T_{2g}(\nu_1)$	-				
11	$[Cu(TP)_4Y_2]$	287	2.090	34843.205	(C-T)	New band	-	-	-	-
		540	0.024	18518.518	$^2b_{1g}\rightarrow{}^2b_{1g}(\nu_3)$	$^2Eg_{1r}\rightarrow{}^2T_{2g}$				
		745	0.060	13422.818	$^2a_{1g}\rightarrow{}^2b_{1g}(\nu_2)$					
12	Ad	219	0.073	45662.1	$\pi\rightarrow\pi^*$	-	-	-	-	-
		273	1.599	36630.036	$\sigma\rightarrow\pi^*$	-				
13	KSCN	235	0.108	42553.191	$\pi\rightarrow\pi^*$	-	-	-	-	-
		266	0.529	37593.985	$n\rightarrow\pi^*$	-				
		232	0.576	43103.448	$\pi\rightarrow\pi^*$, (C-T)	-				
14	$[VO(CA)_2(Ad)X_2]$	296	2.347	33783.783	$^2B_{2g}\rightarrow{}^2A_{1g}(\nu_3)$	New band with corresponding (C-T)	-	-	-	-
		533	0.088	18761.726	$^2B_{2g}\rightarrow{}^2B_{1g}(\nu_2)$	-				
		811	0.174	12330.456	$^2B_{2g}\rightarrow{}^2E_{1g}(\nu_1)$	-				
15	$[Co(CA)_2(Ad)X_2]$	211	0.045	47393.364	-	Blue shift with the Hypo chromic effect	12742.098	971	731.163	0.753
		279	1.712	35842.293	$^4T_{1g}(F)\rightarrow{}^4A_{2g}(\nu_2)$	With corresponding (C-T)				
		408	0.020	24509.803	$^4T_{1g}(F)\rightarrow{}^4T_{1g}(\nu_3)$	-				
		981	0.005	10193.679	$^4T_{1g}(F)\rightarrow{}^4T_{2g}(\nu_1)$	-				
16	$[Ni(CA)_2(Ad)X_2]$	224	0.76	44642.857	(C-T)	With Hyper chromic effect	11323.88	1030	574.74	0.558
		278	1.728	35971.223	$^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)(\nu_3)$	With corresponding (C-T)				
		429	0.007	23310.023	$^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)(\nu_2)$	-				
		480	0.001	20833.333						
		778	0.012	12853.47	$^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)(\nu_1)$					
		906	0.004	11037.527						
		992	0.016	10080.645						
17	$[Cu(CA)_2(Ad)X_2]$	301	2.500	33222.591	(C-T)	New band	-	-	-	-
		351	0.819	28490.028	-	Red shift with Hyper chromic effect				
		365	0.858	27397.26	(C-T)	With Hyper chromic effect				
		496	0.050	20161.29	$^2a_{1g}\rightarrow{}^2b_{1g}(\nu_3)$	$^2Eg_{1r}\rightarrow{}^2T_{2g}$				
		730	0.080	13698.63	$^2a_{1g}\rightarrow{}^2b_{1g}(\nu_2)$					
18	$[VO(TP)_2(Ad)X_2]$	275	1.769	36363.636	(C-T)	With Hyper chromic effect	-	-	-	-
		314	0.213	31847.133	$^2B_{2g}\rightarrow{}^2A_{1g}(\nu_3)$	New bands with corresponding (C-T)				
		325	0.226	30769.23						
		412	0.006	24271.844	$^2B_{2g}\rightarrow{}^2B_{1g}(\nu_2)$	-				
		809	0.012	12360.939	$^2B_{2g}\rightarrow{}^2E_{g}(\nu_1)$					
		816	0.010	12254.902						
		852	0.012	11737.089						
19	$[Co(TP)_2(Ad)X_2]$	218	0.45	45871.559	(C-T)	With Hyper chromic effect	12886.597	971	658.338	0.678
		275	1.720	36363.636	$^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)(\nu_2)$	With corresponding (C-T)				
		526	0.013	19011.405	$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\nu_3)$	-				
		970	0.007	10309.278	$^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)(\nu_1)$	-				
20	$[Ni(TP)_2(Ad)X_2]$	220	0.36	45454.545	(C-T)	With hyper chromic effect	10050.251	1030	855.93	0.831
		275	1.717	36363.636	$^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)(\nu_3)$	With corresponding (C-T)				
		415	0.005	24096.385	$^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)(\nu_2)$	-				
		498	0.006	20080.321		-				
		995	0.002	10050.251	$^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)(\nu_1)$	-				
21	$[Cu(TP)_2(Ad)X_2]$	275	1.798	36363.636	(C-T)	With Hyper chromic effect	-	-	-	-
		480	0.040	20833.333	$^2a_{1g}\rightarrow{}^2b_{1g}(\nu_3)$	$^2a_{1g}\rightarrow{}^2T_{2g}$				
		740	0.086	13513.513	$^2a_{1g}\rightarrow{}^2b_{1g}(\nu_2)$					
22	$[VO(CA)_2(TP)_2XY]$	351	1.087	28490.028	(C-T)	New band	-	-	-	-
		388	1.320	25773.195	$^2B_{2g}\rightarrow{}^2A_{1g}(\nu_3)$	With corresponding (C-T)				
		520	0.077	19230.769	$^2B_{2g}\rightarrow{}^2B_{1g}(\nu_2)$	-				
		814	0.171	12285.012	$^2B_{2g}\rightarrow{}^2E_{g}(\nu_1)$					
23	$[Co(CA)_2(TP)_2XY]$	219	0.157	45662.1	(C-T)	With Hyper chromic effect	13226.847	971	846.712	0.872
		280	1.883	35714.285	$^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)(\nu_2)$	With corresponding (C-T)				
		429	0.017	23310.023	$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\nu_3)$	-				
		904	0.005	11061.946	$^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)(\nu_1)$	-				
		990	0.022	10101.01						
24	$[Ni(CA)_2(TP)_2XY]$	219	0.113	45662.1	(C-T)	With Hyper chromic effect	11266.78	1030	777.65	0.755
		284	1.948	35211.267	$^1A_{1g}\rightarrow{}^1T_{1g}(P)(\nu_3)$	With corresponding (C-T)				
		331	0.017	30211.48	-	Red shift with Hyper chromic effect				
		389	0.029	25706.94	$^1A_{1g}\rightarrow{}^1T_{1g}(F)(\nu_2)$	-				
		807	0.003	12391.573	$^1A_{1g}\rightarrow{}^1T_{2g}(F)(\nu_1)$	-				
		986	0.009	10141.987						
25	$[Cu(CA)_2(TP)_2XY]$	290	2.192	34482.758	(C-T)	New band	-	-	-	-
		567	0.038	17636.684	$^2b_{1g}\rightarrow{}^2b_{1g}(\nu_2)$	$^2Eg_{1r}\rightarrow{}^2T_{2g}$				
		777	0.070	12870.012	$^2a_{1g}\rightarrow{}^2b_{1g}(\nu_1)$					

Table (4) The characteristic infrared absorptions of free ligands and their complexes

	Compound	ν(NH)	ν(OCN) asy	ν(CN)	ν(C=O)	ν(-N=C-)	ν(C-O)	ν(OCN)sy	ν(CS)	δ(M.OCN)	ν(M-N)	δ(M-SCN)	Remark
1	CA	-	-	-	1720 S.b	1658.7 S.b	-	-	-	-	-	-	-
2	KOCN	-	2165.9 V.S	-	-	-	-	1297.4 S	-	-	-	-	-
3	[VO(CA)$_2$Y$_2$]	-	2160 m	-	1700 W.sho	1640 m	-	1220 m	-	590 m	440 m	-	Δν[ν(OCN)$_{asy}$-ν(OCN)$_{sy}$] between (940-1025)Cm^{-1} Δν[ν(-N=C()- ν(-N=C()] ligand CA complexes between (3.7-18.7)Cm^{-1}
4	[Co(CA)$_2$Y$_2$]	-	2260 m.b	-	1710 w.sho	1650 V.S	-	1250 S.b	-	585 S	460 m.b	-	
5	[Ni(CA)$_2$Y$_2$]	-	2260 S.b	-	1715 w.sho	1655 V.S	-	1235 S.b	-	650 S 590 sho	420 W.b	-	
6	[Cu(CA)$_2$Y$_2$]	-	2240 W.b	-	1710 w.sho	1645 V.s	-	1250 S	-	585 S	460 S.b	-	
7	TP	3350 V.W	-	-	1720 S.b	1668.3 S.b	-	-	-	-	-	-	-
8	[VO(TP)$_2$Y$_2$]	3340 w	2140 m	-	1730 Sho	1660 S.b	-	1215 W	-	605W.sh 580 V.w	480 W	-	Δν[ν(OCN)$_{asy}$-ν(OCN)$_{sy}$] between (925-1030)Cm^{-1} Δν[ν(-N=C()- ν(-N=C()] ligand TP complexes between (8.3-33.3)Cm^{-1}
9	[Co(TP)$_2$Y$_2$]	3360 S.b	2240 S	-	1725 W.sho	1650 S.b	-	1210 V.W	-	605W 575 V.w	460 W.b	-	
10	[Ni(TP)$_2$Y$_2$]	3360 S.b	2240 S	-	1730 V.w	1650 W.b	-	1215 W	-	605V.w 580 Sho	480 V.w	-	
11	[Cu(TP)$_2$Y$_2$]	3320 S	2200 M	-	1700 Sho	1635 V.s	-	1205 W	-	600 W 565 V.w	460 m.b	-	
12	Ad	3350 W.sho	-	-	-	1672.2 V.s	1365.5 S	-	-	-	-	-	-
13	KSCN	-	-	2048.3 V.s	-	-	-	-	740.6 V.s	-	-	-	-
14	[VO(CA)$_2$(Ad)X$_2$]	3330 m.b	-	2070 S	1710 Sho	1650 S-b	1350 W	-	640 S	-	565 W 525 W	450 m	Δν[ν(-N=C()- ν(-N=C)] ligand CA complexes between (3.7-23.7)Cm^{-1} Δν[ν(-N=C()- ν(-N=C()] ligand Ad complexes between (17.2-37.2)Cm^{-1} Δν[ν(-C-N()- ν(-C-N)] ligand Ad complexes between (5.5-20.5)Cm^{-1}
15	[Co(CA)$_2$(Ad)X$_2$]	3340 m.b	-	2060 S.sh	1690 Sho	1640 V.s	1355 V.w	-	730 V.w	-	580V.w 560sho 505V.w	430 m.b	
16	[Ni(CA)$_2$(Ad)X$_2$]	3330 m.b	-	2110 m	1700 Sho	1655 V.s	1345 W	-	650 W.b	-	585 V.w 520 V.w	420 m	
17	[Cu(CA)$_2$(Ad)X$_2$]	3320 S	-	2160 m	1690 m	1635 m	1360 V.w	-	660 m	-	575V.w 540V.w 475 W	415 W	
18	[VO(TP)$_2$(Ad)X$_2$]	3330 m.b	-	2030 m	1700 Sho	1640 S.b	1350 W	-	720 V.w	-	595 W 570 V.w 545 V.w	445 W.b	Δν[ν(-N=C()- ν(-N=C()] ligand TP complexes between (3.3-28.3)Cm^{-1} Δν[ν(-N=C()- ν(-N=C()] ligand Ad complexes between (7.2-32.2)Cm^{-1} Δν[ν(-C-N()- ν(-C-N()] ligand Ad complexes between (5.5-15.5)Cm^{-1}
19	[Co(TP)$_2$(Ad)X$_2$]	3320 S.b	-	2130 S.sh	1715 w.sho	1665 S	1360 W	-	690 V.w	-	580m.b 500s.b	410 W	
20	[Ni(TP)$_2$(Ad)X$_2$]	3320 Sho	-	2080 S.sh	1700 Sho	1645 V.s	1355 m	-	735 W	-	590 W 560 W 530 W	420 S	
21	[Cu(TP)$_2$(Ad)X$_2$]	3340 W	-	2070 W	1700 Sho	1650 S	1355 m	-	730 V.w	-	585 V.w 560 V.w 530 V.w	430 m.b	
22	[VO(CA)$_2$(TP)$_2$XY]	3340 S.b	2240 m	2100 S-sh	1700 Sho	1650 V.s	-	1200 m	720 S.b	590 m	540 m	425 m	Δν[ν(OCN)$_{asy}$-ν(OCN)$_{sy}$] between (975-1040)Cm^{-1} Δν[ν(-N=C()- ν(-N=C()] ligand CA complexes between (8.7-58.7)Cm^{-1} Δν[ν(-N=C()- ν(-N=C()] ligand TP complexes between (18.3-68.3)Cm^{-1}
23	[Co(CA)$_2$(TP)$_2$XY]	3320 S.b	2220 m	2060 S.sh	1700 Sho	1600 S.b	-	1205 m	730 W	575 W	500 W	430 W	
24	[Ni(CA)$_2$(TP)$_2$XY]	3340 S.b	2240 m	2080 S.sh	1705 Sho	1640 V.s	-	1225 m	740 m	560 m	535 Sho	440 m.b	
25	[Cu(CA)$_2$(TP)$_2$XY]	3340 S.b	2200 m	2060 S-sh	1705 Sho	1620 V.s	-	1225 m	740 V.w	560 W	535 V.w 505 V.w	415 V.w	

S= strong, m=medium, W= weak , sho= shoulder, sh= sharp, b=broad, V= very, asy= asymmetry, sy=symmetry

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تخليق ودراسة معقدات ذات متكاثرات مختلفة مع بعض العناصر الانتقالية

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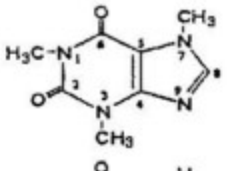
الخلاصة:

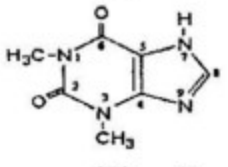
لقد تم في هذا العمل تحضير بعض المعقدات الحاوية على لكاندات مختلطة مع بعض العناصر الانتقالية وهي معقدات جديدة بحسب علمنا وبعد الرجوع الى المعلومات من شبكة الانترنيت ولغاية (2003). وقد تم دراسة وتشخيص هذه المعقدات على أساس التحليل الدقيق لعناصر الكربون، الهيدروجين والنتروجين (C, H, N) وتقدير الفلز كل في معقده وكما استخدمت الدراسات الطيفية كأطياف الاشعة تحت الحمراء I.R وأطياف الاشعة فوق البنفسجية–المرئية U.V-Vis لتشخيص المعقدات فضلا عن قياس التوصيلية المولارية وأخيرا تم قياس الحساسية المغناطيسية للمعقدات وعلى أساس هذه الدراسات أمكن وضع الصيغة العامة لهذه المعقدات والتي صنفت الى خمسة مجاميع وكالاتي:-

1. $[M(CA)_4Y_2]$.
2. $[M(TP)_4Y_2]$.
3. $[M(CA)_2(Ad)X_2]$.
4. $[M(TP)_2(Ad)X_2]$.
5. $[M(CA)_2(TP)_2XY]$.

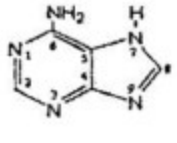
Cu^{+2} ، Ni^{+2} ، Co^{+2} ، VO^{+2} = M^{+2}



Caffeine = CA



Theophylline =TP



Adenine = Ad

(SCN$^-$) Thiocyanate ion = X

(OCN$^-$) Cyanate ion = Y