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Some New Trinuclear Vanillin Schiff Base Complexes of Cobalt, Nickel and Copper

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الخلاصة

أجرينا في هذا البحث تحضير بعض المعقدات ثلاثية النواة المتجانسة وغير المتجانسة للكوبلت والنيكل والنحاس وذلك بمفاعلة كلوريدات او نترات هذه الفلزات مع ليكاند من نوع قاعدة شيف مشتق من الفانلين والمالونيل هيدرازيد. لقد تم الحصول على معقدات بالصيغ العامة: $[M_3(VMH_4)_2X_6)]$, $[M_2M'(VMH_4)_2X_6]$, $[MM'M''(VMH_4)_2X_6]$ و $K_2[M3(VM)_2]$, $K_2[M_2M'(VM)_2]$, $K_2[MM'M''(VM)_2]$ اذ يمثل كل من: M,M',M'' ايونات الكوبلت والنيكل والنحاس الثنائي الموجب و VM ,VMH_4 الشكل المتعادل ورباعي القاعدة لليكاند و X ايون الكلوريد او النترات. تم تشخيص الليكاند ومعقداته بالطرق التحليلية والطيفية والمغناطيسية وبينت هذه الدراسات عمل الليكاند في هذه المعقدات بشكل سداسي السن متعادل وسداسي السن رباعي القاعدة في كل من الوسطين المتعادل والقاعدي ليعطي معقدات سداسية التناسق لها بنية ثماني السطوح ورباعية التناسق لها بنية رباعي السطوح او المربع المستوي، على التوالي. تم ايضا دراسة فترة الاستقرارية وثابت استقرار بعض من هذه المعقدات في المحلول المتعادل وذلك باستخدام طريقة قياس الأطياف الضوئية. لقد اتضح من تعيين النسب المولية بطريقة جوب بان المعقدات تكون بنسبة ١:١ فلز: ليكاند في المحلول (باختلاف ماهي عليه في الحالة الصلبة ٢:٣) كما ان ثوابت الاستقرار متشابهة وذلك لكون العوامل المؤثرة متساوية.

ABSTRACT

In this study homo and hetero trinuclear complexes of cobalt (II), nickel (II) and copper (II) were prepared by the reaction of their salts (chloride and nitrate) with a Schiff base ligand derived from vanillin and malonylhydrazide. Complexes of the general formulae: $[M_3(VMH_4)_2X_6)]$, $[M_2M'(VMH_4)_2X_6]$, $[MM'M''(VMH_4)$2X6] and K2$[M_3(VM)_2]$, $K_2[M_2M'(VM)_2]$, $K_2[MM'M''(VM)_2]$ (where M, M', M" are the dipositive ions of cobalt, nickel and copper, respectively, VMH_4, VM are the neutral and tetra basic forms of the ligand and X= Cl, NO_3) were isolated from both neutral and basic media, respectively. The ligand and its complexes were characterized by using analytical, physical and spectral methods. The studies revealed the hexadentate nature of the ligand which gave hexacoordinated and tetracoordinated metal complexes with the most probable octahedral and tetrahedral or square planar structures in neutral and basic media, respectively. The stability period and the stability constants of some of these complexes in neutral solution have been studied spectrophotometrically. The compositions of the complexes were determined by the use of Job method. The results indicate the formation of only 1:1 metal: ligand complexes with similar stability constants.

INTRODUCTION

The rational design and synthesis of polynuclear coordination complexes, aiming at understanding the structure and chemical factors that govern the exchange coupling between paramagnetic centers are of continuing interest in biology, chemistry and physics [1-3]. Particular interest has recently been focused on the development of super molecular structures created by hydrogen bonds as a new challenge for the synthesis of non-serendipitous species in order to study their magnetic behavior [4-7]. A variety of ligands containing N and O donor atoms have been employed for the preparation of such systems. Among such ligands are the Schiff bases [8-13].

The Schiff base compounds constitute an important class of ligands which have been extensively studied in coordination chemistry, mainly due to their facile synthesis and easily tunable steric, electronic and catalytic properties. Schiff bases having donors such as N_2O_2 and N_4 around the metal ion form complexes of chromium, manganese, nickel and rhenium have been used as catalysts for carbonylation, hydrogenation, hydroformulation and expoxidation reactions [14-17]. Also, N_2O_2 donor Schiff bases and for their role in biological systems [18,19] have been extensively studied as oxygen carriers and as catalysts for water splitting system [20-23]

In the present work, we report the preparation and characterization of a new type of homo- and hetero-trinuclear complexes formed by the reactions of cobalt(II), nickel(II) and copper(II) salts with the Schiff base ligand bis (vanillidene)malonylhydrazide derived from the condensation of vanillin and malonyldihydrazide.

EXPERIMENTAL

Materials and Methods

The chemicals used throughout this work were all of Analar grade used as supplied without further purification. The di-acid hydrazide, malonyldihydrazide was prepared by the reaction of hydrazine hydrate with diethylmalonate 2:1 ratio, according to standard procedure [25]. The Schiff base ligand, bis (vanillidene) malonylhydrazide (VMH_4), was prepared by the condensation of 1:2 ratio of malonyldihydrazide (0.01 mol, 1.32g) and vanillin (0.02 mol, 3.04g) in ethanol. The reaction mixture was refluxed for about 6 hours. Pale yellow precipitate result which was filtered off washed with cold ethanol and dried. The product was characterized by elemental analysis:

MP = 138 ˚C

Found: C, 57.30; H, 5.23; N, 14.26%

$C_{21}H_{20}N_4O_6$ requires: C, 57.00; H, 5.00; N, 14.00%

Preparation of the complexes

Throughout all the preparations 3:2 metal to ligand ratio was always used.

1- Complexes formed in neutral medium: To a solution of the ligand made by dissolving 0.01 mol in 30 ml ethanol a solution of the metal salt containing 0.015 mol in 30 ml ethanol was added. The mixture was refluxed on a water bath for 2-3 hours. After cooling, the precipitated complexes were filtered off, washed with ethanol and dried in vacuum desiccators.
2- Complexes formed in alkaline medium: An ethanolic solution of the ligand (0.01 mol in 30 ml ethanol) was made alkaline by the addition of 0.1 N KOH, then a solution containing 0.015 mol of the metal salt in 30 ml ethanol was added slowly within 30 minutes. An excess of KOH (few drops) was added to the mixture until complete precipitation. The mixture was then digested on a water bath for about 10 minutes and left to cool. The separated complexes were filtered off, washed with ethanol and dried in vacuum desiccators.

Analyses and physical measurements

The ligand and its complexes were analyzed for carbon, hydrogen and nitrogen by using Perkin-Elmer 2400 analyzer at the School of Chemistry, University of Birmingham-UK, while cobalt, nickel and copper measured gravimetrically using standard methods [26]. Conductivity measurements were carried out on 10-3 M solutions in dimethylformamide (DMF) using LF-42 digital conductivity meter at room temperature. Infrared absorption spectra were recorded on recorded on IR-300 and Pye-Unicam SP-1100 infrared spectrophotometers on the range of 400-4000 cm^{-1} using KBr discs, at the College of Science, University of Salahaldean- Erbil. The measurements were performed on the sample in the form of KBr discs. The electronic spectra were recorded on a Shimadzu UV-Vis 160 A spectrophotometer for 10^{-3} M solutions in dimethylformamide at room temperature, using 1 cm quartz cell. Melting points were measured by using Gallenkamp melting point apparatus at the range 0 to 350 ˚C. The magnetic susceptibility measurements were made by the Faraday method at 25 ˚C using a Bruker BM6 instruments. Diamagnetic corrections were calculated using Pascal's constants [27].

Determination of stability constant

The conditional stability constants of some of the complexes were estimated spectrophotometrically by the following method: solutions containing exactly 3:2 proportion of the metal salt to the ligand were prepared. Then the low absorbance (Es) of these solutions was measured. Similar solutions were then prepared containing the same amount of the metal salt, but with excess ligand. In this case it was assumed that the complex is largely associated and consequently it had a higher absorbance (Em). The difference between the absorbance represented a measure of the degree of dissociation (α) of the complex [28] which given by

$\alpha = Em\text{-}Es / Em$

The stability constants (K) were calculated by using the following equation:

$K = 1 - \alpha / 4\alpha^3 C^2$ (where C represent the concentration).

Results and Discussion

The following equations explain the reactions of the metal salts with the ligand and showing the formation of the complexes in both neutral and alkaline medium.

1- Neutral medium reactions:

$$3MX_2.nH_2O + 2VMH_4 \longrightarrow [M_3(VMH_4)_2X_6] + 3nH_2O$$

$$2MX_2.nH_2O + M'X_2.mH_2O + 2VMH_4 \longrightarrow [M_2M'(VMH_4)_2X_6] + (2n+m)H_2O$$

$$MX_2.nH_2O + M'X_2.mH_2O + M''X_2.yH_2O + 2VMH_4 \longrightarrow [MM'M''(VMH_4)_2X_6] + (n+m+y)H_2O$$

2- Alkaline medium complexes:

$$3MX_2.nH_2O + 2VMH_4 + 8KOH \longrightarrow K_2[M_3(VM)_2] + 6KX + (8+3)nH_2O$$

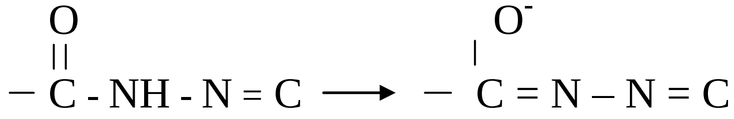
$$2MX_2.nH_2O + M'X_2.mH_2O + 2VMH_4 + 8KOH \longrightarrow K_2[M_2M'(VM)_2] + 6KX + (8+2n+m)H_2O$$

$$MX_2.nH_2O + M'X_2.mH_2O + M''X_2.yH_2O + 2VMH_4 + 8KOH \longrightarrow K_2[MM'M''(VM)_2] + 6KX + (8+n+m+y)H_2O$$

Where M, M', M'' are the dipositive ions of cobalt, nickel and copper, respectively, VMH_4, VM are the neutral and tetra basic forms of the ligand, X = Cl^- or NO_3^- and n, m = 6, y = 2, 3.

As indicated in the above equations, neutral complexes resulted from neutral medium, while anionic species obtained from alkaline medium reactions. In all cases 3:2 metals to ligand proportion was found and confirmed by the different studies conducted on these complexes, as shown by the analytical data given in Table 1. All the complexes are stable in dry air at room temperature and have relatively high melting or decomposition points (above 350 °C). They are insoluble in water, cold ethanol and methanol but they are slightly soluble in dimethylformamide (DMF). The low molar conductance for the neutral complexes in this solvent indicate their non-ionic nature, while the conductance values for the basic medium species suggested 2:1 electrolytic nature [29], Table 1. The stability constants were studied only for the neutral complexes but the other type precipitated on addition of alkali and thus prevents the measurements. The values shown in Table 1 reflect the similar stability of these complexes which most probably due to the same environments for all of them.

The coordination sites were concluded by comparison of the infrared absorption spectra of the ligand and its complexes, Table 2. The band due to C=O stretching mode lowered in neutral complexes by about 18-35 cm^{-1} and disappeared in anionic complexes due to deprotonation of the enol form of the ligand. This was confirmed by the disappearance of the N-H bands due to the following tautomerism:



$$-\overset{\overset{O}{\|}}{C}-NH-N=C \longrightarrow -\overset{\overset{O^-}{|}}{C}=N-N=C$$

These observations suggested coordination through both carbonyl oxygen atoms for the neutral complexes [30,31] and enolic oxygen atoms for the anionic complexes [32,33]. In both types of complexes the azomethine (C=N) band lowered by about 15-30 cm^{-1} suggesting coordination through both azomethine nitrogen atoms [34]. The OH bands lowered by about 55-100 cm^{-1} for neutral complexes suggesting coordination through both hydroxyl oxygen atoms and disappeared for anionic complexes indicating that coordination took place through both phenoxy oxygen atoms, Table 2, [35, 36], since the C-O band which occurred in the ligand spectrum at 1210 cm^{-1} lowered in the spectra of these complexes by about 20 cm^{-1} and appeared around 1190 cm^{-1}. Neutral complexes showed three bands due to NO_3 groups (ν_3,ν_1,ν_5) at 995-1525 cm^{-1}, Table 2. The positions of these bands and the difference between the two bands of higher frequencies (130-150 cm^{-1}) suggest monodentate action of nitrate groups in these complexes. Bands due to Cl ion could not be observed as such bands occur below 300 cm^{-1} which is out of our spectrophotometer range. For anionic complexes no band due to NO_3 was found in their spectra which indicate the absence of NO_3 groups from these complexes. This observation is in a good agreement with the conductance data and the suggested formulations. In addition, new bands were observed in the spectra of all complexes at about 420-430 and 460-480 cm^{-1} and attributed to the stretching modes of M-O and M-N, respectively [36].

Table 3 gives the electronic spectral data and the suggested structures of the prepared complexes. The neutral hexa-coordinated cobalt and nickel complexes showed three bands in the visible region which attributed to high-spin octahedral symmetry. These bands due to the allowed transitions, $^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$ (ν_2), $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ (ν_3) and $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$ (ν_2), $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$ (ν_3) for cobalt and nickel complexes, respectively. For the hexa- coordinated copper complexes only one band was observed (Table 3) and attributed to the three combined transitions $^2B_{1g} \longrightarrow {}^2A_{1g}$, $^2B_{1g} \longrightarrow {}^2B_{2g}$, $^2B_{1g} \longrightarrow {}^2E_g$. Since this band is broad, asymmetrical and below 1500 cm^{-1}, therefore distorted (Jhan-Teller distortion) octahedral structure was suggested [37].

For the neutral mixed metal complexes that contain both cobalt and nickel, three bands were also observed for each metal ion and attributed to octahedral structure. For the mixed metal complexes of cobalt or nickel with copper, four d-d bands were observed in their spectra, three of them due to the allowed transitions for cobalt or nickel and the fourth one due to the allowed transition for copper ion. Figure I represent the electronic spectrum for the complex $[Co_2Cu(VMH_4)_2(NO3)_6]$ as an example for the spectra of such compounds. The electronic spectra of the mixed metal complexes containing cobalt, nickel and copper ions were also studied. Such spectra are very complicated as seven bands were expected but some of them are located at nearly the same region. The calculated ratio of ν_2/ν_1 for cobalt complexes (1.32-1.35) and for nickel complexes (1.54-1.63) confirms the octahedral structure [38]. The low value of β (0.28-0.33) for cobalt complexes refer to the high proportion of covalence, while the higher value (0.72-0.78) for nickel complexes indicates the low covalent character, Table 3, [39]. In the spectra of the anionic species only one band was observed for cobalt, nickel and copper complexes, located at 13945-14822cm^{-1} for cobalt and at 13184-13600 cm^{-1} for nickel complexes. This band is due to $^4A_2(F) \longrightarrow {}^4T_1(P)$ (ν_3) and $^3T_1(F) \longrightarrow {}^3T_1(P)$ (ν_3) transitions in tetrahedral field. The other two bands, ν_1 and ν_2, are located at the lower part of the spectra, therefore could not be observed due to the instrument limitation. Figure II shows the spectrum of $K_2[Co_2Ni(VM)_2]$ were two bands appeared, one for cobalt and the other for nickel, representing ν_3 for each ion. Again, one band for anionic copper complexes was appeared in the region around 19157-19410 cm^{-1}. This band is due to the two combined transitions $^2B_{1g} \longrightarrow {}^2A_{1g}$ and $^2B_{1g} \longrightarrow {}^2E_g$, therefore square planar structure was suggested for these tetracoordinated complexes.

The presence of charge transfer bands are due to π-π^* transition and observed for all the complexes. These bands indicate the presence of certain amount of π-bonding that due to the back donation as the ligand contains empty π^*-orbital. The values of CFSE are ranging between 9258-12456, 11900-12456 and 7936-8536 cm^{-1} for cobalt, nickel and copper complexes in octahedral field, respectively, indicating that nickel complexes have the highest stabilization energy and copper complexes have the lowest values.

The magnetic moments for all the complexes are given in Table 2. The values for cobalt complexes (4.19-4.48 BM) are in good agreement with that expected for high-spin octahedral and tetrahedral environments for cobalt(II), d^7-system indicating the presence of three unpaired electrons. The values of the magnetic moments for hexa-coordinated and tetra-coordinated nickel(II) complexes (2.39-2.98 BM), Table 2, indicate the presence of two unpaired electrons (high-spin d^8-system) and thus, confirming the tetrahedral structure for the tetra-coordinated Ni(II) complexes. The relatively low values of the magnetic moments for cobalt and nickel complexes are probably due to antiferromagnetism resulting from the interaction of the adjacent metallic centers, known as the super exchange mechanism [40]. In case of copper(II) complexes the values of the magnetic moments (2.42-2.46 BM) are corresponding to the presence of one unpaired electron (d^9-system). The little high values are expected to be due to orbital contributions and/or, in some cases to super exchange mechanism either through the interaction of Cu^{+2}……Cu^{+2} or by the involvement of the ligand causing ferromagnetic behavior [41, 42]. The values magnetic moments agreed well with the proposed structures and the number and positions of the electronic spectral bands observed in the visible region for these complexes [38].

For all the other complexes containing more than one metal ion, the values of the magnetic moments agreed well with the high-spin character which represents the resultant of the individual moment for each ion. In all cases the values are lower than would be expected which is due as mentioned above, to the antiferromagnetic behavior.

The nature of the complexes and the stability constant (ranging between 1.09×10^4 - 1.79×10^4) for some of those prepared in neutral medium were studied in solution (the study can not be conducted for the anionic complexes since they are precipitated upon addition of alkali). 1:1 metal to ligand ratio was obtained and all the species have similar stability constants as the environmental factors surrounding the metal ions are nearly the same. Since all the complexes are high-spin, therefore, the effects of CFSE on the stability constants are the same for all the complexes.

Conclusion

From the different studies conducted on the ligand and its complexes and from the given data, the following conclusion can be drawn: The ligand acts as hexa-dentate in both neutral and basic media (Figures III and IV). High-spin octahedral complexes obtained from neutral solution, while tetra-coordinated complexes with tetrahedral structure for cobalt and nickel complexes and square planar structure for copper complexes resulted from alkaline solution. The study of the nature of the complexes in solution showed the formation of only 1:1 mononuclear species. This is occurred due to the weak HO - M bonding which couldn't stabilize the trinuclear framework in solution in comparison to the solid state.

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Table 1- Analytical data and some physical properties

Compound	Ω_M cm^2 ohm^- mol^- in DMF	Colour	MP C°	μ_{eff} (BM)	Analysis %, Found (Calculated)				
					C	H	N	M	Cl
1-$[Co_3(VMH_4)_2(NO_3)_6]$	37	Pale yellow	230	4.19	33.68 (33.81)	3.12 (2.97)	14.68 (14.53)	13.16 (13.10)	
2-$[Co_3(VMH_4)_2\ Cl_6]$	25	Pale brown	231	4.48				14.50 (14.85)	17.60 (17.88)
3-$[Ni_3(VMH_4)_2(NO_3)_6]$	38	Pale green	208	2.39	34.02 (33.83)	3.12 (2.97)	14.41 (14.54)	13.01 (13.06)	
4-$[Ni_3(VMH_4)_2\ Cl_6]$	40	deep yellow	242	2.92				14.62 (14.86)	17.71 (17.89)
5-$[Cu_3(VMH_4)_2(NO_3)_6]$	30	deep yellow	232	2.46	33.61 (33.47)	2.80 (2.94)	14.22 (14.38)	14.0 (13.92)	
6-$[Cu_3(VMH_4)_2\ Cl_6]$	29	Pale brown	275	2.48				15.70 (15.84)	17.40 (17.67)
7-$[Co_2Ni(VMH_4)_2(NO_3)_6]$	35	Pale green	276	3.53				Co,8.69(8.33) Ni,4.65(4.35)	
8-$[Ni_2Co(VMH_4)_2(NO_3)_6]$	25	Pale green	270	2.98				Ni,8.69(8.73) Co,4.56(4.35)	
9-$[Co_2Cu(VMH_4)_2(NO_3)_6]$	38	Pale green	266	3.23				Co,8.40(8.64) Cu,4.72(4.66)	
10-$[Cu_2Ni(VMH_4)_2(NO_3)_6]$	40	Pale brown	271	3.11				Cu,9.40(9.35) Ni,4.31(4.32)	
11-$[CoNiCu(VMH_4)_2(NO_3)_6]$	34	Yellow	256	3.86				Co,3.85(4.35) Ni,4.51(4.35) Cu,4.71(4.69)	
12-$K_2[Co_3(VM)_2]$	150	dark brown	314	4.22				16.55 (16.87)	
13-$K_2[Ni_3(VM)_2]$	140	Brown	310	2.98				16.75 (16.87)	
14-$K_2[Cu_3(VM)_2]$	139	dark yellow	320	2.42	43.20 (42.99)	3.18 (3.02)	10.75 (10.56)	17.87 (17.96)	
15-$K_2[Co_2Ni(VM)_2]$	152	Yellowish green	311	3.51				Co,11.38(11.25) Ni,5.51(5.60)	
16-$K_2[Ni_2Co(VM)_2]$	146	Yellowish green	298	3.64				Ni,11.29(11.21) Co,5.72(5.62)	
17-$K_2[Co_2Cu(VM)_2]$	156	Dark brown	330	3.59				Co,11.39(11.20) Cu,6.15(6.04)	
18-$K_2[Cu_2Ni(VM)_2]$	140	Dark brown	286	3.12				Cu,12.41(12.03) Ni,5.62(5.55)	
19-$K_2[CoNiCu(VM)_2]$	143	Brown	302	4.02				Co,5.51(5.60) Ni,5.70(5.58) Cu,6.12(6.04)	

Table 2- Some important infrared spectral data (cm^{-1}).

Table 2- Some important infrared spectral data (cm^{-1}).

Neutral compound	$\nu_{(OH)}$	$\nu_{(NH)}$	$\nu_{(C=O)}$	$\nu_{(C=N)}$	$\delta_{(OH)}$	$\nu_{(N-N)}$	$\nu_{(M-N)}$	$\nu_{(M-O)}$	$\nu(NO_3)$
VMH_4	3480	3204	1660	1600	1290	998	-----	-----	---------
$[Co_3(VMH_4)_2(NO_3)_6]$	3400	3205	1640	1580	1260	1033	460	425	998,1385,1515
$[Co_3(VMH_4)_2\ Cl_6]$	3380	3200	1640	1585	1240	1034	470	420	-------
$[Ni_3(VMH_4)_2(NO_3)_6]$	3400	3210	1640	1580	1265	1034	470	420	1000,1385,1518
$[Ni_3(VMH_4)_2\ Cl_6]$	3400	3205	1640	1580	1270	1033	465	430	--------
$[Cu_3(VMH_4)_2(NO_3)_6]$	3400	3200	1640	1580	1265	1025	460	430	1000,1385,1518
$[Cu_3(VMH_4)_2\ Cl_6]$	3400	3200	1642	1580	1265	1025	470	430	----------
$[Co_2Ni(VMH_4)_2(NO_3)_6]$	3400	3205	1635	1585	1260	1035	460	425	998,1385,1520
$[Ni_2Co(VMH_4)_2(NO_3)_6]$	3405	3200	1640	1580	1265	1030	465	430	1000,1380,1518
$[Co_2Cu(VMH_4)_2(NO_3)_6]$	3425	3220	1625	1570	1275	1030	480	430	998,1380,1515
$[Cu_2Ni(VMH_4)_2(NO_3)_6]$	3420	3205	1635	1570	1270	1033	470	420	998,1375,1525
$[CoNiCu(VMH_4)_2(NO_3)_6]$	3400	3205	1635	1570	1265	1025	460	425	1000,1380,1518

Anionic complexes	$\nu_{(C=N)}$	ν(azine) -C=N-N=C-	$\nu_{(C-O)}$	$\nu_{(N-N)}$	$\nu_{(M-N)}$	$\nu_{(M-O)}$
$K_2[Co_3(VM)_2]$	1580	1585	1160	1025	460	425
$K_2[Ni_3(VM)_2]$	1580	1590	1160	1023	470	420
$K_2[Cu_3(VM)_2]$	1585	1595	1160	1025	460	425
$K_2[Co_2Ni(VM)_2]$	1570	1588	1160	1030	465	425
$K_2[Ni_2Co(VM)_2]$	1575	1590	1160	1030	460	425
$K_2[Co_2Cu(VM)_2]$	1570	1585	1160	1030	470	425
$K_2[Cu_2Ni(VM)_2]$	1585	1600	1160	1025	460	420
$K_2[CoNiCu(VM)_2]$	1580	1600	1160	1020	460	425

Table 3- The electronical Spectral data for some of the complexes

Compound	ν_1	ν_2	ν_3	C.T	$10D_q$	β	ν_2/ν_1	CFSE	Structure
$[Co_3(VMH_4)_2(NO_3)_6]$	10730	14393	23364	33112	12634	0.337	1.34	10107	Octahedral
$[Co_2Ni(VMH_4)_2\ Cl_6]$	10800 10220	14315 16664	23662 26814	31604 32415	12405 10220	0.312 0.782	1.32 1.63	10212 11906	Octahedral for Co &Ni
$[Ni_3(VMH_4)_2(NO_3)_6]$	10037	16129	26315	35714	10037	0.758	1.61	12044	Octahedral
$[Cu_3(VMH_4)_2\ Cl_6]$	13525	-----	-----	32110	13525	----	----	81225	Octahedral
$[Co_2Cu(VMH_4)_2(NO_3)_6]$	10650 13227	14370	22222	33988 31152	11572 13227	0.281	1.35	9258 7936	Octahedral for Co&Cu
$[CoNiCu(VMH_4)_2(NO_3)_6]$	10380 10630 14306	---- 16420 ----	22138 26460 ----	31430 34384 30120	12058 10630 14306	---- 0.72 ----	---- 1.54 ----	---- 12456 8536	Octahedral for Co, Ni & Cu
$K_2[Co_3(VM)_2]$	----	----	13945	32635	----	----	----	----	Tetrahedral
$K_2[Ni_3(VM)_2]$	------	------	13333	32051	-----	------	----	-----	Tetrahedral
$K_2[Co_2Ni(VM)_2]$	----- -----	---- ----	14822 13184	32051 30816	----- -----	---- ----	---- ----	---- ----	Tetrahedral for Co & Ni
$K_2[Cu_3(VM)_2]$	19410	----	----	32115	19410	----	----	----	Sq. Planar
$K_2[Co_2Cu(VM)_2]$	---- 19157	---- ----	14534 ----	32154 30516	---- ----	---- ----	---- ----	---- ----	Co-Oct. Cu-Sq.
$K_2[CoNiCu(VM)_2]$	---- ---- 19337	---- ---- ----	14326 13600 ----	32020 35460 30416	---- ---- ----	---- ---- ----	---- ---- ----	---- ---- ----	Co,Ni-Tet. Cu-Sq.

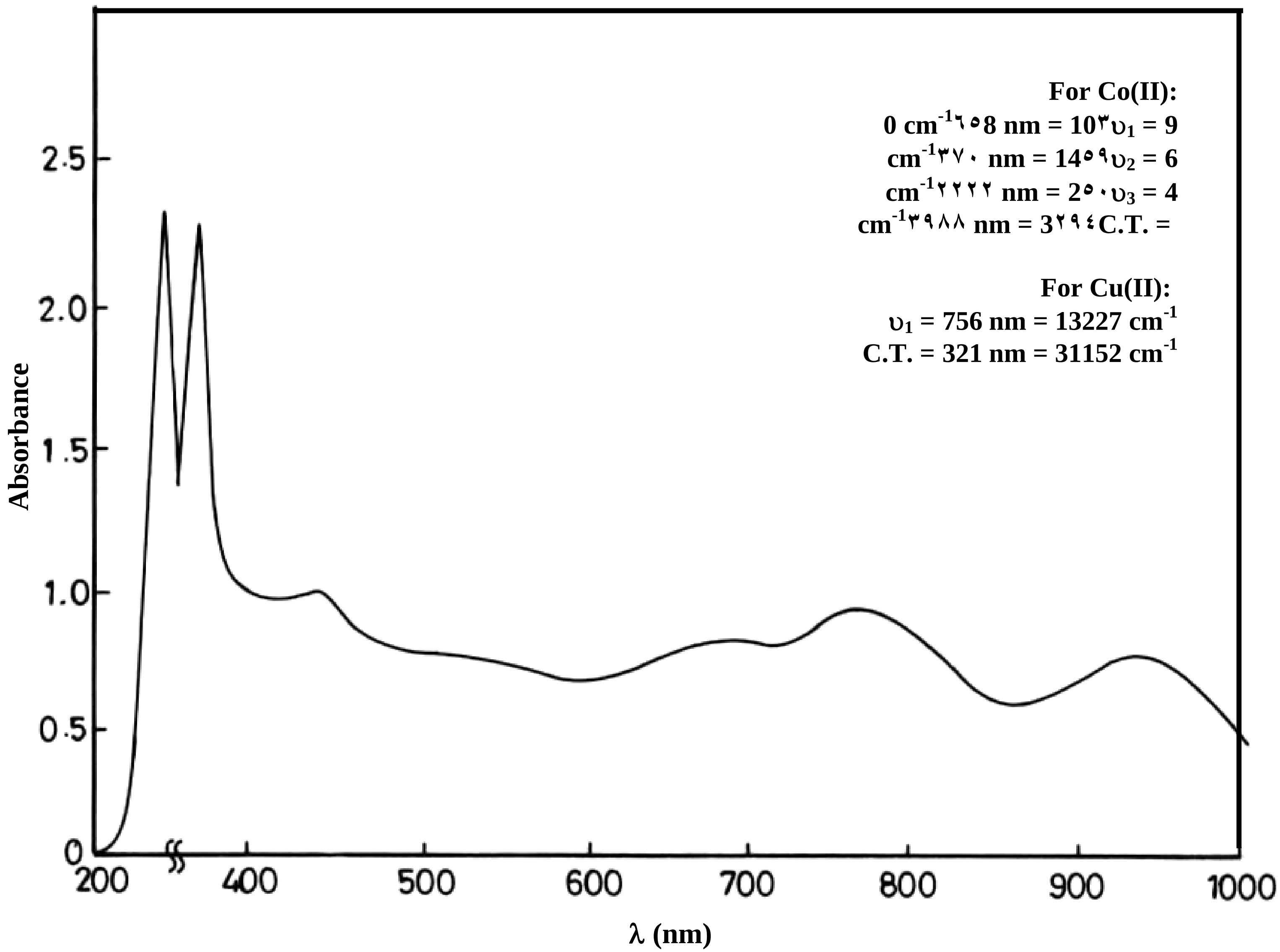


Fig.I-Electronic spectrum of $[Co_2Cu(VMH_4)_2(NO_3)_6]$

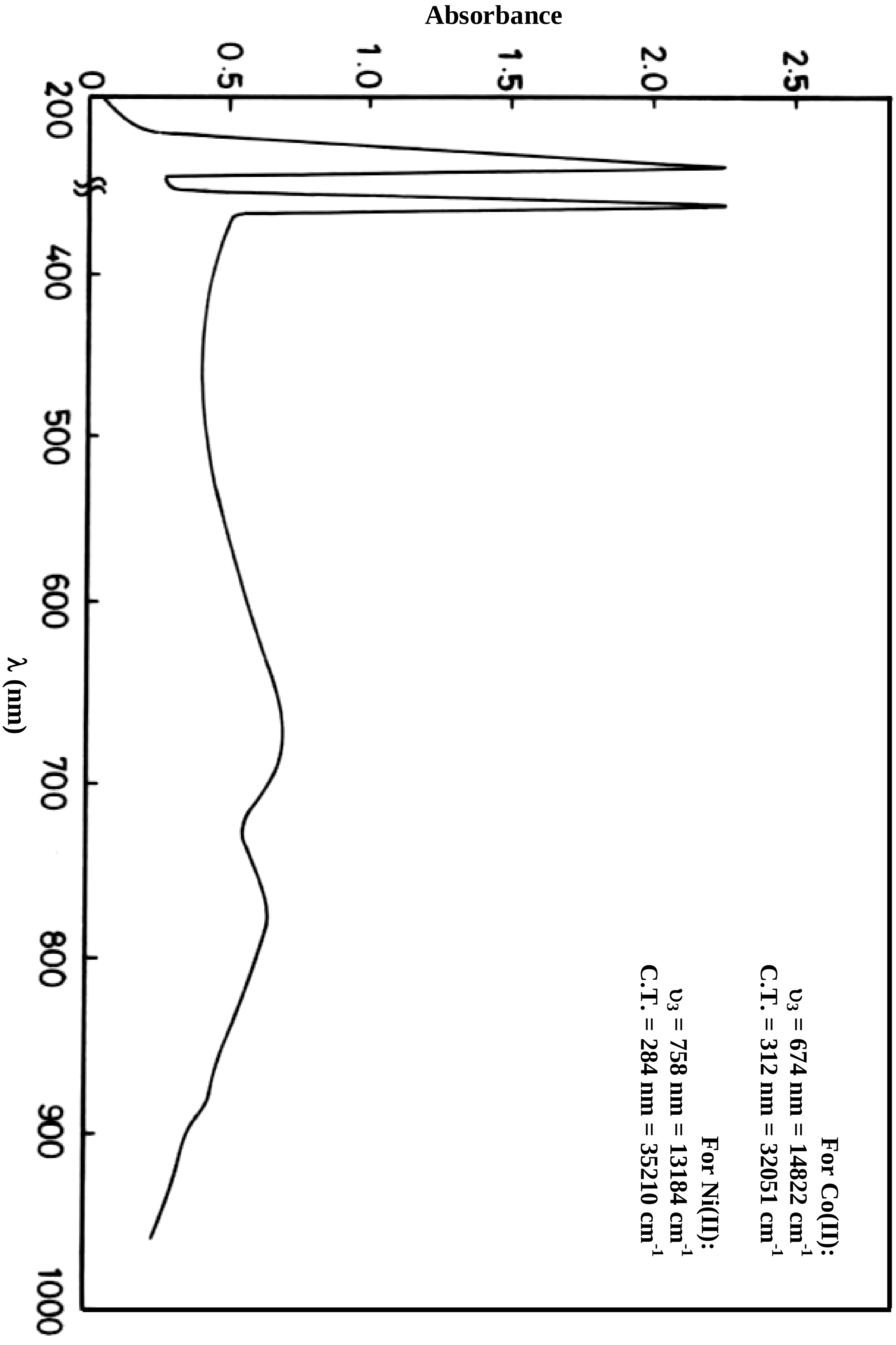
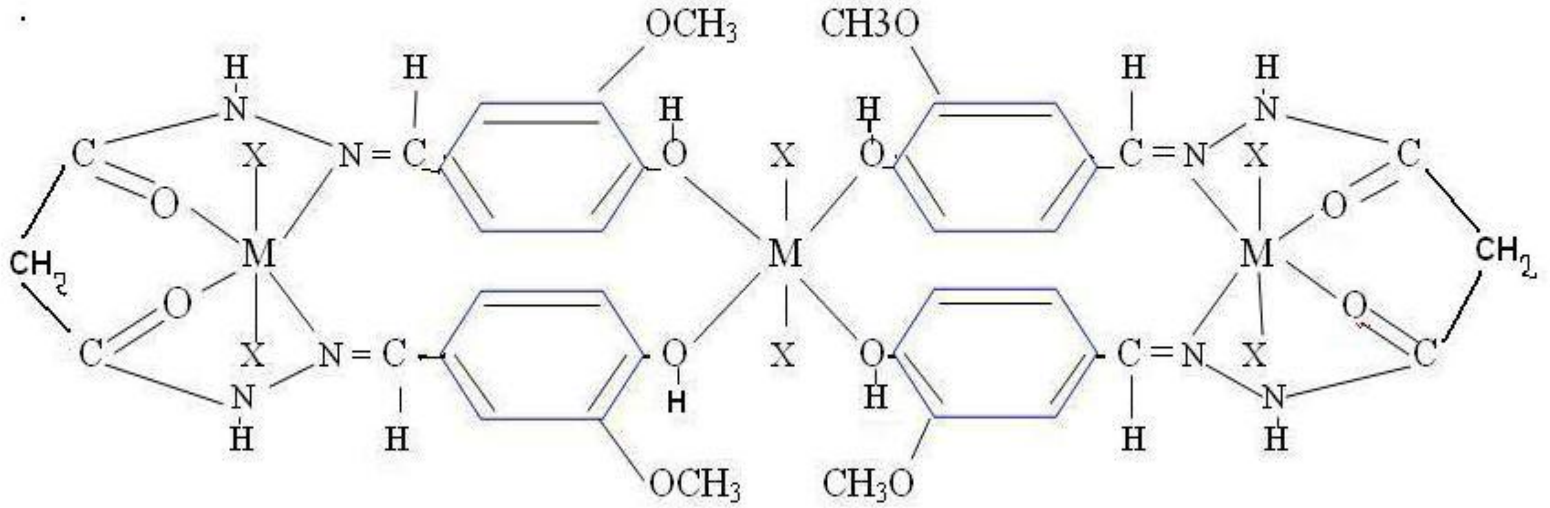


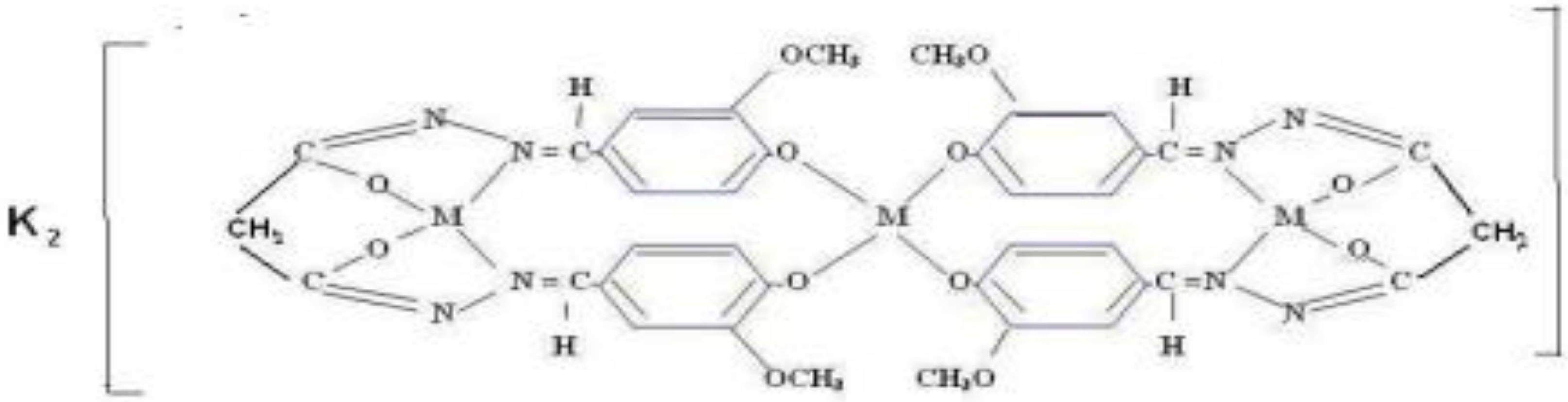
Fig. II- Electronic spectrum of $K_2[Co_2Ni(VM)_2]$



M= The dipositive ions of cobalt, nickel and copper.

X= The anion of Cl or NO_3

Fig. III. Neutral complexes of the ligand VMH_4 .



M– The dipositive ions of cobalt, nickel and copper.

Fig. IV. Anionic complexes of the ligand VM^{-4} .