PREPARATION AND IDENTIFICATION OF SOME PVA –METAL COMPLEXES

Nada Ali Al-Najjar
Department of Chemistry, College of Science for Women, University of Baghdad. Baghdad- Iraq

Abstract

Some metal complexes of Poly (vinyl alcohol) (PVA) of the formula $[M(PVA\text{-}oxi)_2 (NO_3)_2]$ [M= Mn(II), Fe(II), Co(II) and Ni(II)] and vanadyl complex with formula $[VO(PVA\text{-}oxi)_2SO_4]$ were prepared and characterized by atomic absorption, IR, UV-Vis spectroscopic techniques, molar conductance, magnetic susceptibility as well as the relative viscosity.

It was found that the prepared complexes were formed only with partially oxidized PVA, which has carbonyl and hydroxylic groups through PVA chains and then react with metal ion in N,N-dimethylformamide as a solvent in (1:2) molar ratio (metal : Ligand) in neutral or slightly basic solution.

The results showed that the ligand (PVA-oxi) was bidentate ligand coordinated with metal ion through the oxygen atoms of carbonyl and hydroxylic groups of its chain, with an octahedral geometry around the metal ions for all the complexes.

The prepared polymeric complexes are thermally stable (above 360°C) which inhanced their industrial applications.

تحضير وتشخيص بعض معقدات متعدد فنيل الكحول

ندى علي النجار
قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد. بغداد – العراق.

الخلاصة

تم تحضير بعض معقدات متعدد فنيل الكحول (PVA) ذات الصيغة $[M(PVA)_2 (NO_3)_2]$ حيث ان $Ni^{2+} , Co^{2+}, Fe^{2+}, Mn^{2+} = M$ ومعقد الفناديل ذو الصيغة $[VO(PVA)_2 SO_4]$ وتشخيصها من خلال طيف الأمتصاص الذري، طيف الأشعة تحت الحمراء، الأشعة فوق البنفسجية–المرئية، التوصلية المولارية والحساسية المغناطيسية بالاضافة الى اللزوجة النسبية.

وجد ان المعقدات المحضرة يتم الحصول عليها من خلال الأكسدة الجزيئة لمتعدد فنيل الكحول PVA الذي يحتوي على مجموعة الكاربونيل والهيدروكسيل على السلسلة الجانبية للـ PVA ومن ثم مفاعلته مع الأيون الفلزي في مذيب داي مثيل فورمامايد (DMF) وبنسبة مولية(2:1) (فلز : ليكاند) في وسط متعادل أو قاعدي ضعيف.

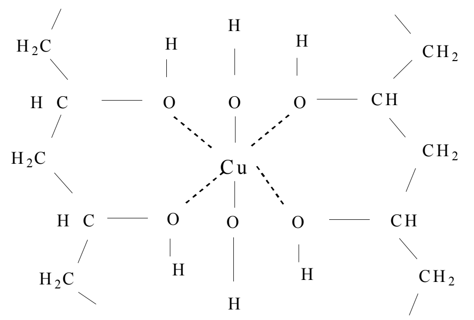
بينت النتائج ان الليكاند متعدد فنيل الكحول المؤكسد اكسدة جزيئة (PVA-oxi) يسلك كليكاند ثنائي السن إذ يتناسق مع الأيون الفلزي من خلال ذرات الأوكسجين لكل من مجموعتي الكاربونيل والهيدروكسيل بشكل ثماني السطوح حول الأيون الفلزي لجميع الأيونات الفلزية المستخدمة.

ان المعقدات البوليمرية المحضرة تمتلك ثباتية حرارية أعلى من360^{o}م وهذه الخاصية تشجع على استخدامها في التطبيقات الصناعية.

Introductions

Synthesis of polymeric ligand and the selective chelation of specific metal ions is a field of active research [1]. The metal ions of polymer complexes have potential applications such as electrolytes [2], sensory [3], stabilizers [4] and semiconducting [5].

A number of ligands including polydentate amines, crown-ethers, porphyrine, phosphines, bipyridines and naphthyridines have been bound with mainly polystyrene and polystyrene-divinyl benzen copolymers [6-9]. The most important polymer was polyvinyl alcohol (PVA), some of metal complexes of this polymer have been synthesized [10, 11]. The Cu (II) complex of (PVA) (scheme 1) in a neutral or slightly basic solution [12]. formed, the copper doped polyvinyl alcohol which has been used in multidimensional applications in holography optics and mechanically flexible systems [13].



Scheme 1

In this paper we investigate the preparation and characterization of some metal complexes of polyvinyl alcohol.

Experimental

1- Materials

The PVA used has a molecular weight of 20000 partially hydrolyzed 80%, was supplied from B.D.H. The metal salts $VOSO_4$ $.5H_2O$, $Mn(NO_3)_2.6H_2O$, $Fe(NO_3)_2.4H_2O$, $Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$ (all from B.D.H.) were commercially pure samples. Concentration of hydrogen peroxide (H_2O_2) used in this work was (20V). Other solvents were distilled before use.

2- Apparatus

Melting points were determined by using (STUART.SCINTIFIC) melting point SMP1. U.V-Visible spectra in DMF at room temperature were recorded on a Shimadzu U.V-Visible double beam scanning spectrophotometer 260. I.R spectra (4000-200 cm^{-1}) were recorded as CsI discs on a pye-Unicam SP3-100 I.R spectrophotometer. Metal contents of the complexes were determined using GBC 933 Atomic Absorption spectrophotometer. Electrical conductivity of 10^{-3} M solution of complexes in DMF at room temperature were obtained by using ELEKTP. LEITFA. HIGKEIT conductometer. Magnetic susceptibility measurements were carried out by using Johnson Mattey Catalytic Systems. Viscosity measurements were carried out by using Capillary viscometer type Ostwald Viscometer at 30C°and DMF as a solvent.

3- Oxidation of PVA

In a 250ml round-bottom flask equipped with a reflux condenser, a thermometer and dropping funnel 15 .2 gm, (0.2 mmol) of PVA with 100 ml of water as a solvent were placed. Then 20 ml of H_2O_2 20% vol was added from dropping funnel, with stirring and the mixture was refluxed for 3hrs. The oxidized PVA was formed ,the solvent was evaporated and the oxidized polymer was dried under vacuum at 50ºC.

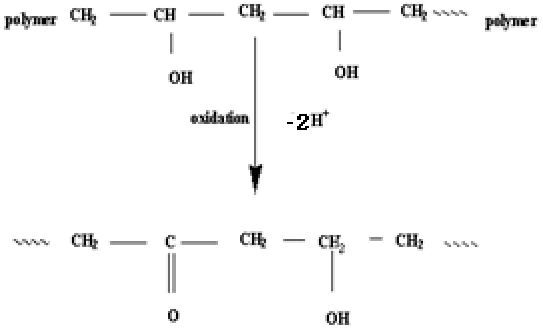
4- Synthesis of oxidized PVA- Complexes

In a 100ml two neck round bottom flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet tube, 2mmol of oxidized PVA was dissolved in 10 ml DMF, then 1 mmol of metal salt in DMF in each case was added.

The mixture was heated under reflux for a bout 10 hrs. Colored products were formed in neutral or slightly basic solution. The products were filtered and purified by washing with ethanol, then dried at 50 °C in an oven overnight.

Results and Discussion

The PVA was oxidized in the presence of hydrogen peroxide at (60-100°C) to form a mixture of carbonyl and hydroxyl group in the polymeric chain as is shown in scheme (2).



Scheme 2

The decomposition of all the prepared (PVA–oxi) metal complexes were higher than 360°C. This indicates that the presence of metal ion increases the thermal stability of the polymer.

The results of atomic absorption analysis are given in table (1), along with the corresponding theoretical values. The percentage of metal in each complex suggest a 1: 2 metal: ligand structure.

Viscosities were measured for all the prepared (PVA–oxi) complexes in DMF as a solvent at 30°C, ŋrel was measured for 1% concentration.

Physical properities with metal analysis and viscosities of (PVA – oxi) and its metal complexes are listed in table (1).

Spectral studies

Infrared (I.R) Spectra

The prominent infrared absorption along with the assignments of the ligand (PVA–oxi) and metal complexes are presented in table (2).

The I.R spectrum of the ligand (PVA–oxi), as in (figure 1). shows a slightly broad band at 3420 cm-1 and another band at 1050 cm^{-1} these bands were assigned to ʋ (OH) and ʋ (C-OH) stretching vibration respectively [14,15]. The same bands appeared in the metal complexes spectra, but shifted to higher frequencies in the rang 3500-3450 cm^{-1} and 1150-1090 cm^{-1} respectively [16] as shown in (figures 2).

The carbonyl group in the ligand exhibited a band at 1740 cm^{-1}, this band was shifted to lower frequencies by 80-40 cm^{-1} in the metal complexes [15, 16, 17]. These shifts of ʋ(OH) and ʋ (C = O) may be due to the coordination to metal ion [15, 16,17].

The I.R spectrum of the ligand also shows a band at 2780 cm^{-1} due to the intramolecular hydrogen bonding between the carbonyl and OH groups [14] which has disappeard in the spectra of metal complexes.

Additional peaks were observed in the spectra of complexes in the region 250-265 cm^{-1}, 463-535 cm^{-1} and 1020-1060 cm^{-1} and were attributed to ʋ (M-O) of the ONO_2 group [16], (C= O)[16] and (covalent OH) [18,19] group respectively. The V (IV) complex showed a broad bands at 960 and 850 cm^{-1} which can be assigned to ʋ (V = O) + ʋ (V–O) vibration modes respectively [20,21,22]. The vibrational modes of SO_4^{2-} group in this complex exhibited a medium intensity band at 438 cm^{-1} which can be attributed to the υ_2, the absence of υ_1 and splitting of υ_3=1050, 1135 and υ_4 = 660, 650, unidentate coordination behaviour of SO_4^{2-} in vanadyl complex [23].

Electronic Spectra, Magnatic Moments and Electrical Conductivity Measurements

The absorption bands and assignments related to the ligand and its complexes with magnetic moments and molar conductance are listed in table (3).

The electronic spectrum of the ligand (PVA.oxidized) (Figure 3), consists of a high intensity band appeared in the U.V region at wave number 36363.6 cm^{-1}(275 nm), this band is attributed to intra ligand $\pi\rightarrow\pi^*$ transition [14] Another band of lower intensity appeared near the visible region 30769 cm^{-1} (325 nm) this band was attributed to $n\rightarrow\pi^*$ [14] .

Complexation with metal ions was confirmed by the appearance of new bands in the visible and near I.R regions which were assigned mainly to charge transfer and d–d transitions.

The molar conductance data show that all the complexes are non-electrolytes in DMF [24] indicating that the chelating ligand are covalently bonded in all cases.

[Mn(PVA.oxi)$_2$(NO$_3$)$_2$]: The electronic spectrum of the Mn(II) complex exhibited a band at 30303 cm^{-1} (330 nm) which can be attributed to the charge transfer (C.T) and another band was observed in the 17301 cm^{-1} (578 nm) which was assigned to
$^6A_1g\rightarrow{}^4T_2g$ [25]. The magnetic moment μeff = 6.05 B.M. refers to the octahedral geometry about Mn(II) ion [26].

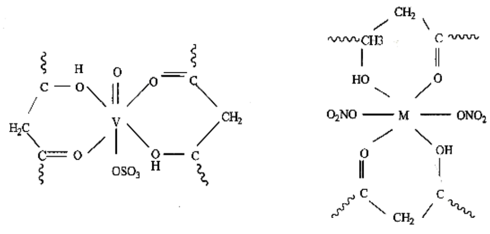
[Fe(PVA.oxi)$_2$(NO$_3$)$_2$]: The spectrum of this complex exhibited a weak intensity band in the 12360.9 cm^{-1} (809 nm) which may be reasonable to the $^5T_2g\rightarrow{}^5Eg$ transition consistent with an octahedral geometry around the Fe(II) ion [25]. The magnetic moment μeff = 5.32 B.M. gives another evidence for the octahedral geometry around Fe(II) ion [26].

[Co(PVA.oxi)$_2$(NO$_3$)$_2$]: The elecrronic spectrum of this complex Figure (4) shows three bands at 22255 cm^{-1} (449 nm), 19607.8 cm^{-1} (510 nm) and 10893 cm^{-1} (918 nm) which can be assigned as
$^4T_1g(F) \rightarrow {}^4T_1g(p)$ (υ_3) mixed with (C.T),
$^4T_1g(F) \rightarrow {}^4A_2g(F)$ (υ_2)
and

$^4T_1g(F) \rightarrow {}^4T_2g(F)$ (υ_1) respectively [25]. The observed magnetic moment μeff = 4.70 B.M. further illustrated the octahedral geometry around Co (II) ion [26].

[Ni(PVA-oxi)$_2$(NO$_3$)$_2$]: The electronic spectrum of this complex (Figure 5) shows two bands at 25575 cm^{-1} (319 nm) and 15267 cm^{-1} (655 nm) which were assigned to $^3A_2g(F)$ $^3T_1g(p)$ (υ_3) mixed with charge transfer → $^3T_1g(F)$ (υ_2) → (C.T) and to ^3A_2g transitions respectively [15 ,25], related to octahedral Ni(II) complex, the band appeared at 13315.5 cm^{-1} (751nm) is assigned to the forbidden transition ^3A_2g ^1Eg [25]. Applying the ratio $\upsilon_3/\ \upsilon_2$ on Tanaba –Sugano diagram of Ni (II) complexe [25]. The value of υ_1 was calculated as 9092 cm^{-1} (1099.8 nm). μeff = 3.7B.M. [26].

[VO(PVA.oxi)$_2$SO$_4$]: The spectrum of VO^{2+} complex suggest an octahedral environment of vanadyl complex .The former have three distinct bands at 732(nm)13661cm^{-1}, (597)16750cm^{-1} and (472)21153cm^{-1} which an be assigned as $^2B_2 \rightarrow {}^2E\ \upsilon_1$, $^2B_2 \rightarrow {}^2B_1(\upsilon_2)$
And $^2B_2 \rightarrow {}^2A_1$ (υ_3) respectively [25], and the magnetic moment μeff = 1.7 B.M. gives additional evidence for the octahedral structure of VO^{2+} (IV) complex [26].
According to these observations and those based on UV–Visible absorption spectra, I.R spectra, the structures of the complexes can be suggested as follows(Figure6).



[VO (PVA.OXi)$_2$ SO$_4$]

[M(PVA.OXi)$_2$(NO$_3$)$_2$]
M= Mn (II)
Fe(II),Co(II)
Ni(II).

Figure 6: The proposed structural fomula of [M(PVA-oxi)$_2$(NO$_3$)$_2$and [VO(PVA.oxi)$_2$SO$_4$

Table 1: physical proprieties, metal analysis and viscosities of PVA .oxidized and metal complexes

Comp. No.	Compound	Color	m.p^{o}c (decom.)	Yield%	Metal analysis cacl.(found)M%	Ŋrel dL/gm
1	(PVA.oxi)	white	240	84.2	__	1.2
2	[Mn(PVA.oxi)$_2$(NO$_3$)$_2$]	White	>360	62.8	15.02 (17.42)	1.43
3	[Fe(PVA.oxi)$_2$(NO$_3$)$_2$]	Yallow	>360	48.1	17.23 (18.1)	1.55
4	[Co(PVA.oxi)$_2$(NO$_3$)$_2$]	Red	>360	58.4	18.0 (20.1)	1.48
5	[Ni(PVA.oxi)$_2$(NO$_3$)$_2$]	Green	>360	60.3	17.9 (15.8)	1.58
6	[Vo(PVA.oxi)$_2$SO$_4$]	Dark – brown	>360	32 . 2	16.50 (16.71)	1.56

Table 2: I.R Vibrational frequencies (cm^{-1}) of the of PVA–oxidized and metal complexes

Comp. No.	Compound	ν (OH)	ν (C =O)	ν (C-OH)	ν M-ONO$_2$ (VO-OSO$_3$)	ν M-OH	ν M-O
1	Ligand PVA.oxi	3420	1740	1050	_	_	_
2	[Mn(PVA.oxi)$_2$(NO$_3$)$_2$]	3465	1680	1145	250	1060	620
3	[Fe(PVA.oxi)$_2$(NO$_3$)$_2$]	3500	1710	1090	265	1025	650
4	[Co(PVA.oxi)$_2$(NO$_3$)$_2$]	3433	1720	1120	255	1045	655
5	[Ni(PVA.oxi)$_2$(NO$_3$)$_2$]	3450	1700	1140	250	1045	623
6	[VO (PVA.oxi)$_2$ SO$_4$]	3455	1665	1090	ν_2=438 ν_3 = 1050,1135 ν_4 = 660, 650	1065	640 960

Table 3: Electronic spectra ,molar conductance and magnetic moment (μeff = B.M.) of the ligand and metal complexes

Comp. No.	Compound	Band position cm^{-1}	Assignments UV - Visible	Conductivity Λm $cm^{-1}.ohm^{-1}\ mol^{-1}$	μ_{eff} B.M.
1	Ligand (PVA.oxi)	υ_1=30769 υ_2=36363	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	–	–
2	$[Mn(PVA.oxi)_2(NO_3)_2]$	υ_1=17301 υ_2=30303	$^6A_1g \rightarrow {}^4T_2g$ C.T	25.04	6.01
3	$Fe(PVA.oxi)_2(NO_3)_2]$	υ_1 =12360	$^5T_2g \rightarrow {}^5Eg$	20.4	5.32
4	$[Co(PVA.oxi)_2(NO_3)_2]$	υ_1=10893 υ_2=19607 υ_3=22255	$^4T_1g_{(F)} \rightarrow {}^4T_2g_{(F)}$ $^4T_1g_{(F)} \rightarrow {}^4A_2g_{(F)}$ $^4T_1g_{(F)} \rightarrow {}^4T_1g_{(P)}$	22.8	4.70
5	$[Ni(PVA.oxi)_2(NO_3)_2]$	υ_1=10998 υ_2=15267 υ_3=25575	$^3A_2g_{(F)} \rightarrow {}^3T_2g_{(F)}$ $^3A_2g_{(F)} \rightarrow {}^3T_1g_{(F)}$ $^3A_2g_{(F)} \rightarrow {}^3T_1g_{(P)}$	25.9	3.7
6	$[VO(PVA.oxi)_2SO_4]$	υ_1=13661 υ_2=16750 υ_3=21153	$^2B_2 \rightarrow {}^2E$ $^2B_2 \rightarrow {}^2B_1$ $^2B_2 \rightarrow {}^2A_1$	28.1	1.7

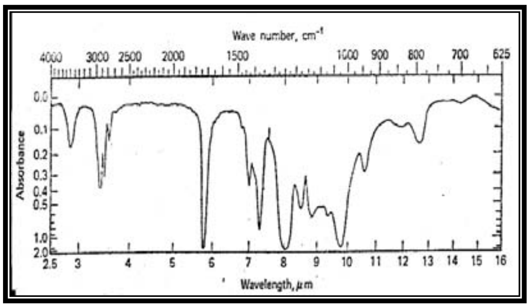


Figure 1:Infrared spectrum of ligand (PVA-oxidized)

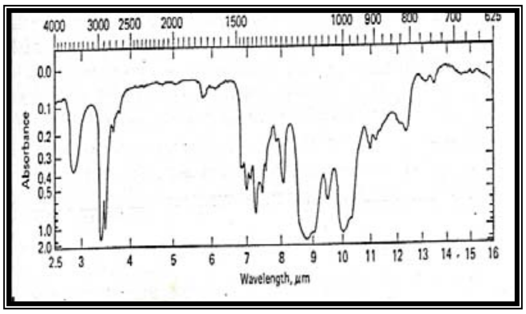


Figure 2:Infrared spectrum of complex$[Fe(PVA.oxi)_2(NO_3)_2]$

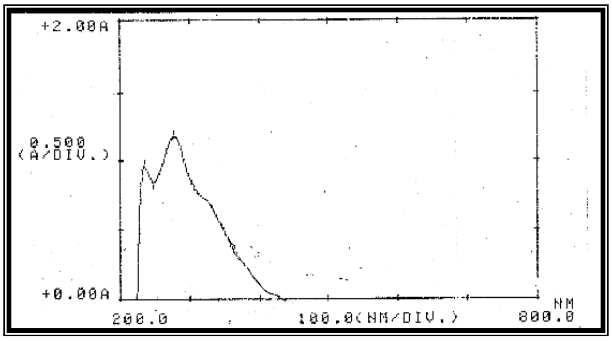


Figure 3: Electronic spectum of ligand (PVA-oxidized)

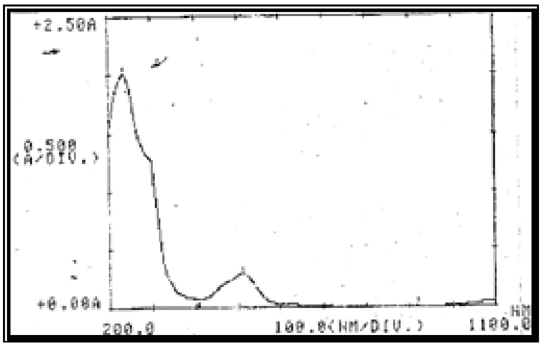


Figure4: Electronic spectum of complex [Co (PVA.oxi)$_2$(NO$_3$)$_2$]

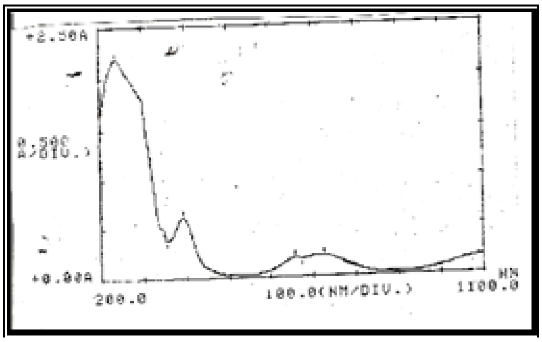


Figure5: Electronic spectum of complex [Ni(PVA.oxi)$_2$(NO$_3$)$_2$]

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