Synthesis and Characterisation of Novel Cobalt(II),Copper (II) and Mercury (II) Complexes of Poly Vinyl Urethanised Oxime.

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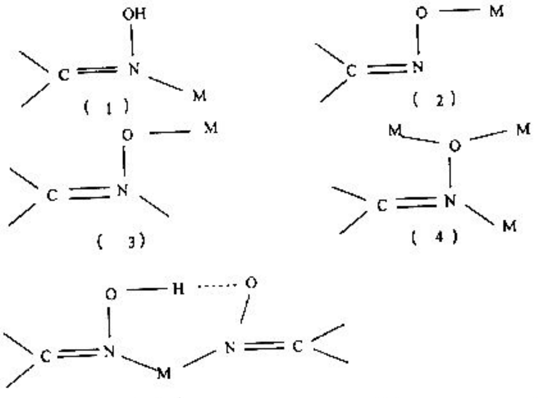
Abstract

The reaction of poly (vinyl alcohol) (PVA) with Urea in (DMSO) resulted in uerthanised oxim, which reacted with diacetylmonoxime in a (DMSO/methanol) to give anew type (N_2) polymeric bidentate imine oxime ligand [HL] , The ligand was reacted with MCl_2 (where M= Co, Cu, and Hg). Under reflux in a (DMF/Methanol) mixture with (1:1) ratio to give Complexes of the general formula [M $(L)_2$]X, (where M= Co,Hg, Cu). All compounds have been characterized by spectroscopic methods [IR, U.V.-Vis, Atomicabsorption] microanalysis along with conductivity measurements, from the above data the proposed molecular structure for Co,Cu, and Hg is a distorted. Tetrahedral

Introduction

Oxime or oximato species can bind a metal in different coordination modes and exhibit versatiler activity (1) ,scheme(1)



Much information has accumulated in areas such as structure , stability, and reactivity of the molecule , analytical chemistry and biochemical models(2-4).Awide variety of tetradentate imine oxime ligand type N_4 with a variety of substituents on the backbone and their complexes have been made on the cobalt (II)-cobalt (III)-bis(dimethylglyoxime) system which has been called a model system for the B_{12} moiety (5).The important roles of such oxime complexes lies in their activity as,polymers catalyses, fungicides and bactericides (6).This paper reports the synthesis and characterization of new poly vinyl urethanised oxime ligand derived from the reaction of poly (vinyl alcohol) with urea in DMS Oresulted urethanised ,which reacted with diacetylmonooxime and its cobalt, copper and mercury complexes.

Experimantal

Reagents were purchased from Fluka, Merck, and Redial. Dehan AG-seelze- Hamnover chemical Co. IR spectra were recorded as (KBr) disc using (8300) (FT.IR) Shimadzu spectra photometer electronic spectra of the prepared compounds were measured in the region (200-900) nm for10^{-3} mole. L^{-1}. Solution in (DMSO) at (25) °C using a Shimadzu U.V-Vis spectrophotometer with a quartz cell of (0.1) cm length. Elemantal micro analysis were performed on a (C.H.N) analyzer, model 1106 (carlo-Ebra). While Metal contentes of the complexes were determined by atomic absorption (A.A) technique. Using a Shimadzu (A.A)680 G atomic absorotion spectra photometer. The chloride contains for complexes were determined by using potentiometric titration method. On (686titro processor-665 Dosimat-Metrohm Swiss). Electrical conductivity measurements of the complexes were recorded at (25)° C for 10^{-3} mole.L^{-1} solutions of the samples in (DMSO)using a ten way Ltd. 4071 digital conductivity meter

Preparation

Synthesis of the ligand [HL]

The ligand was prepared by two routes

Route A: The ligand was prepared in two step:

-Preparation of urethanised poly (vinly alcohol) (U-PVA) this was prepared according to littrature method (7), by treating urea with

(PVA) as follows: A (500 ML) three-neeked round bottomed flask, equipped with a stirrer, a condenser, and a thermomerter was charged with (2.8g, 0.2mmole) of (PVA), (25 ML) of dimethtlsulfoxide (DMSO),and (3.8g,63.3mmole) of urea. The contents of the flask were heated under reflux for (3) hrs. The stirred mixture was allowed to cool to room temperature, and by adding (MeOH), and then dried under vacuum. Yield (2.6g) (87%)

-Preparation of the oxime-polymer ligand asolution of diacetylmonoxime (0.77g,7.13mmole) in methanol (10) ml and (2.3) drops of (HBr 48%) was added slowly to amixture of (0.5g, 0.032mmole) of (U-PVA) in dimethylsulfoxide (15ml).The reaction mixture was refluxed for (2) hrs.

The mixture was allowed to cool to room temperature, and by adding methanol (25ml),a yellow-brown gel was formed. Which was collected by filtration, washed twice with methanol (10ml) and dried under vacuum to give the ligand as a yellow-brown solid- yield (0.49g), (84%) (200) °C dec.

Route B:The ligand was prepared in two steps

- **Preparation of the oxime-urae** A solution of diactylmonoxime (2.8g,27.7mmole) in methanol (15ml)and (2.3) drops of (HBr48%) was added slowly to amixture of(2.8g,46.66mmole) of urea in methanol (15ml). The reaction mixture was refluxed for (2)hrs. The mixture was allowed to cool to room temperature, and a white solid was formed which collected by filtration, recrystallised from methanol, and dried under vacuum to give a yelloe-brown solid, yield (3.4g), (87%).

- Preparation of the ligand

A(500) ml three-necked round bottomed flask, equipped with a stirrer, a condensed and a thermometer was charged with (0.3g, 0.021mmole)of oxime-urea.

The contents of the flask were heated under reflux for (3) hrs. The stirred mixture was allowed to cool to room temperature, and by adding 2-propanol, a yellow-brown gel was formed, which was collected by filtration washed with 2-propanol (10)ml, ether (10)ml and dried under vaccum to give the ligand as yellow-brown solid. Yield (0.2 g) 80% (200) °C dec

Synthesis of [Co (L)2] X complex.

A solution of cobalt (II) chloride hexahydrate (0.25g, 1.05m e) in methanol (10) ml was added slowly to a stirred solution igand (0.5g, 0.027mmole) in dimethylformamide (10)ml. The ulting mixture was heated under reflux for (2) hrs during which the solution became a blue in coloure. The resulting mixture was precipitated into methanol (20) ml. A blue gel was formed this was collected by filtration, washed with methanol, ether and dried under vacuum to give (0.43g) (80%) (225)°C dec of the title compound as blue solid

Synthesis of[Cu(L)$_2$] X complex

The method used to prepare the complex [Cu(L)$_2$] was similar to that used for [Cu (L)$_2$]x complex, using copper(II) chloride dehydrate (0.2g,1.176mmole) in place of $CoCl_2.6H_2O$ The quantities of other reagents used were adjusted according. An identical work-up procedure was used to give (0.48g) (88%) of the title compound as a green solid. (250)°C dec.

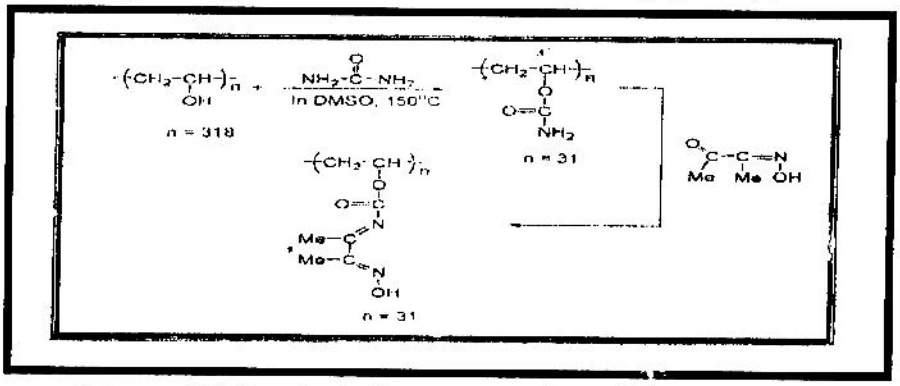
Synthesis of [Hg (L)$_2$] X complex

The method used to prepare the complex [Hg (L)$_2$]X was similar to that employed to prepare complex [Co(L)$_2$]X, using mercury (II) chloride (0.35g, 1.289mmole) in place of $CoCl_2.6H_2O$.The quantities of other reagents used were a djusted accordingly. An identical work-up procedure was used to give (0.42g) (70%) of the title compound as a white solid (245)°C dec.

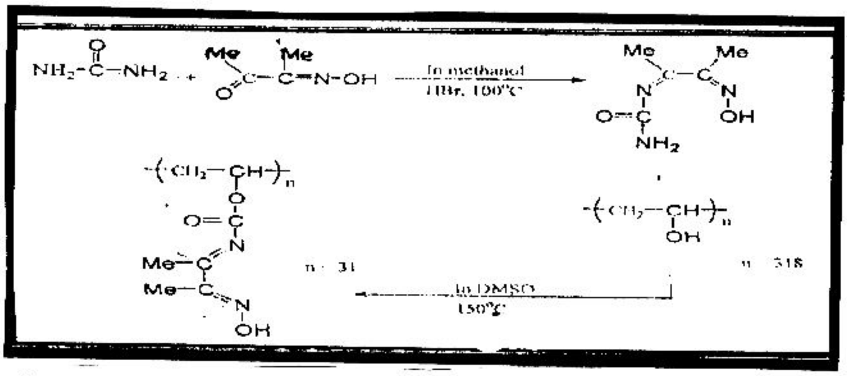
Rusults and Discussion

Synthesis of the ligand

The new oxime (N_2) type ligand (HL) was prepared in two routes according to the general method shown in scheme(2), and (3).



Scheme (2) Route-A-for preparation of ligand



Scheme (3) Route-B-for preparation of ligand

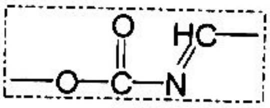
The(I.R) spectrum of the ligand (HL) Fig (2) shows a broad band in (3270-3570)cm^{-1} rang which assigned to several peaks, γ (O—H) stretching for oxime groups, and hydrogen Bonding (intramolecular) and (intermolecular) respectively for polymer (8).The bonds at (1655), (1628) cm^{-1} are due to γ(C=N) from imine and oxime groups respectively. The bands at (937)cm^{-1}, (1103) cm^{-1} and (1710)cm^{-1}are due to γ(N—O), γ(C—O),and γ(C=O) stretching respectively(8) while [u.v-vis] spectrum Fig (3) exhibits a high intense absorption band. (277nm) (37037cm^{-1}) ξmax = 1491 molar^{-1} cm^{-1}), and a shoulder at (350nm) (285741cm^{-1}) (ξmax 250molar^{-1}.cm^{-1}) which assigned to ($\pi \longrightarrow \pi^*$) and ($n \longrightarrow \pi^*$) transitions respectively (9).

Synthesis of the Complexes

The reaction of [HL] with [$MCl_2.XH_2O$] where M=Co, Cu, and Hg in (DMF/methanol) mixture under reflux resulted in the synthesis of the complexes. These complexes are stable in solution and non electrolytes table(3). The analytical and physical data table(l), and spectral data (Table 2,3) are compatible with the suggested structures Fig.(l). The (I.R) spectra of the complexes are presented in table (2). In (3535-3548, 3470-3457)and (3413-3415) cm^{-1}are due to intra and intermolecular hydrogen bonding for polymer and/or water molecular with oxygen of the oximato and for (C=O)group.

The strong bond in free ligand at (1655) cm^{-1}and (1628) cm^{-1}for the γ (C=N) for the imine and oxime groups are shifted to (1619,1429),

(1618, 1496), (1617, 1430)cm^{-1} for this compounds repectively. This can be attributed to the delocalization of metal electrons density in the ligand π-system (10).
The γ(C=O) stretching band at (1710) cm^{-1} for the free ligand are shifted to lower frequencies and appeared at (1640, 1659, 1637) cm^{-1} for compounds this can be attributed to the delocalization of electrons of (C=O) along.



Due to resonance (11). The bands at (410,488), (435,460) and (442,468) $^{cm-1}$ were assigned to γ(M—N) for this compounds respectively (12,13) indicating that the imine and oxime nitrogen' s where involved in coordination with metal ions (14).Figs (2a), (2b)and (2c) represented. The (I.R) spectra of [Co $(L)_2$]X ,[Cu $(L)_2$]X and [Hg $(L)_2$]X.
The (u.v-Vis) spectra of the complexes displayed absorptions of (266-350)nm assigned for ligand field and charge transfer transitions. In [Co$(L)_2$]X complex. The band at (670),(678) nm is attributed to (δ . δ) electronic transitions ($^4A_2 \longrightarrow {}^4T_{1(p)}$) and ($^4A_2 \longrightarrow {}^4T_{1\ (F)}$) suggesting a tetrahedral of structure fig (3a), in [Cu$(L)_2$]X complex the band at (650) nm is attributed to (δ . δ) electronic transitions ($^2B \rightarrow {}^2E$) suggesting a distorted tetrahedral (15).The moler

conductance of the complexes were measure die in (DMSO), table (1), indicating their non electrolytic nature for all complexes (16).

References

1. Singh, A.; Gupta, V. D.; Srivastava, G. and Mehrotra, R.C. (1974). J. Organomet. Chem., 64,145.
2. Fristskii, I.O. (1990). Ph. D. Dissertation, state university of kier 20,101.
3. wey, S.P.; Ibrahime, A.M.; Green, M.A. and Fanwiek, P.E. (1995). Polyhedron, 41, 1097.
4. Skopenko, V.V. ; Fristskii, I.O. ; Lempleka, R.D. and Iskenderov, T.S. (1993). Russ. J. Inorg. Chem., 38, 1827.
5. Schrauzer, G.N. and Windga ssen, R.J. (1967). J.Amer. chem., Soc, 89:1,143.

6.Uzoe,Y.;Yagi, K.; Nakamura, M.; Akamatsu, M.; Miyake,T. and Matsumura,F. (2000). National Journal of Chemistry and Physiology 66: (2) 92-104.
7. Sakurada, I.; Nakajima, A. and Shibatani, K. (1964). Journal of polymer science. A2, 3545.
8. Socrates, G. (1980). "Infrared characteristic gronfreguencies" wiley, New York.
9. William kemp (1987). "inorganicspectroscopy" 2nd.Edition.
10. Hadzi, D. and Premru, L. (1967). spectrochim. Acta, A23, 35.
11. Mosa, T.M.; M.S.C (2002). Militry College of Enginerring.
12. Nakamto, K. (1996) "Infrared spectra of Inorganic and coordination compounds" 4th. Ed., wiely New York.
13. Ferrato, J. (1998). "low frequency vibrations of Inorganic and coordination compounds" plenum, polish J. chem.… 72,519.
14. Tabl, A.S.EI. and lkasher, T. (1998). polishj. Chem.. 72, 519.
15. Silverstein, R.M.; Bassler, G. C. and Morrill, T.C. (1981).4th Ed., J. wiley and sons. 6, 180.
16. Geary, W.J. (1971). Coord. Rev., 7, 81.

Table (1) Analytical and Physical data of the ligand and its complexes

Compound	M.wt	Yield %	m.p(°C)	Color	Found, (Calc) %				
					C	H	N	Cl	Metal
Ligand (HL)	18006.8	84	200 dec	Yellow-brown	(52.97) 52.92	(8.29) 8.2	(4.94) 49.11	-------	-------
$[Cu(L)_2]X$ X=1.7	19484.38	79.6	225 dec	Blue	(48.96) 48.93	(7.83) 7.8	(4.56) 4.52	NiL	(4.81) 4.72
$[Cu(L)_2]X$ X=1.7	19557.6	88.8	250 dec	Green	(48.77) 48.93	(7.80) 7.78	(4.55) 4.51	NiL	(5.16) 5.12
$[Hg(L)_2]X$ X=1.9	21736.78	70.0	245 dec	White	(43.88) 43.86	(7.02) 6.45	(4.09) 3.97	NiL	(14.62) 14.47

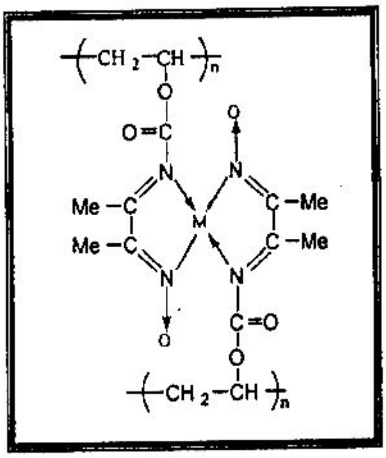
(dec): decomposed (cal.): calculated

Table (2) I.R spectral data of the ligand and its complexes

Compound	γ (O-H)	γ (C=N)imine γ (C=N)oxime	γ (N-O)	γ (C=O)	γ (C-O)	γ (H-O….H) δ (H-O….H)	γ (O-H) Aliph	γ (N-M)
Ligand	(3570,3412) (3470.3270) For polymer	1655 1628	937	1710	1103	2346 1870	2925	----------
$[Co(L)_2]$ X	3540,3460 3415,3265 Poly	1619 1429	980	1640	1025	2050 1735	2853 2925	410 488
$[Cu(L)_2]X$	3548,3475 3413.3235 Poly	1617 1430	989	1637	1035	2060 1805	2845 2925	442 468
$[Hg(L)_2]X$	3548,3470 3413,3250 Poly	1618 1430	995	1638	1037	2120 1716	2845 2924	412 468

Table (3) Electronic spectra data, conductance measurement of ligand (HL) and its complexes.

Compound	λ nm	$\bar{\gamma}$ Wave number cm^{-1}	Σ max Molar^{-1} cm^{-1}	Assignment	$\wedge$ (Ω^{-1} cm^{-1} mol^{-1}	Solvent
HL (ligand)	277 350	36101 28571	9141 250	$\pi \longrightarrow \pi^*$ $n \longrightarrow \pi^*$	--------	--------
[Co(L)$_2$] X	277 610 678	36101 16393 14749	495 100 139	Ligand filed $^4A_2 \longrightarrow {}^4T_1(P)$ $^4A_2 \longrightarrow {}^4T_1(F)$	26	DMSO
[Cu(L)$_2$] X	282 350 650	34560 28571 15384	2123 510 100	Ligand filed charge transfer $^2B_2 \longrightarrow {}^2E$	22	DMSO
[Hg(L)$_2$] X	266	37593	989	Charge transfer	6.1	DMSO



Where:
M= Co(II), x = 27.2, Cu(II), x = 27.3 , Hg(II), x = 30.3

Figure (1) The proposed structure of the complexes.

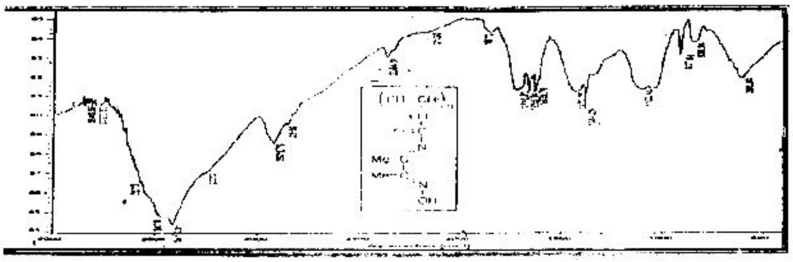


Figure (2) Infrared spectrum of ligand

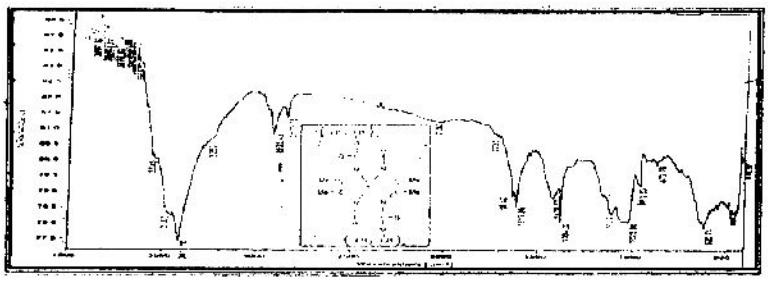


Figure (2a) Infrared spectrum of $[Co(L)_2]X$.

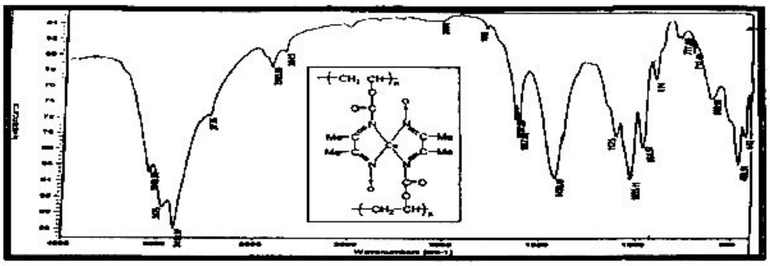


Figure (2b) Infrared spectrum of $[Cu(L)_2]X$.

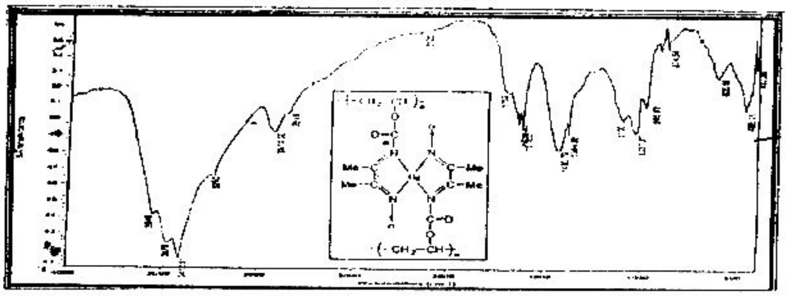


Figure (2c) Infrared spectrum of $[Hg(L)_2]X$.

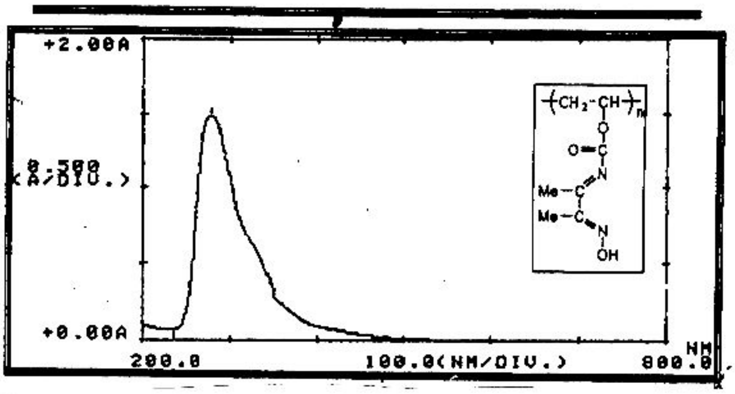


Figure (3) The U.V-Vis spectrum of the ligand (HL).

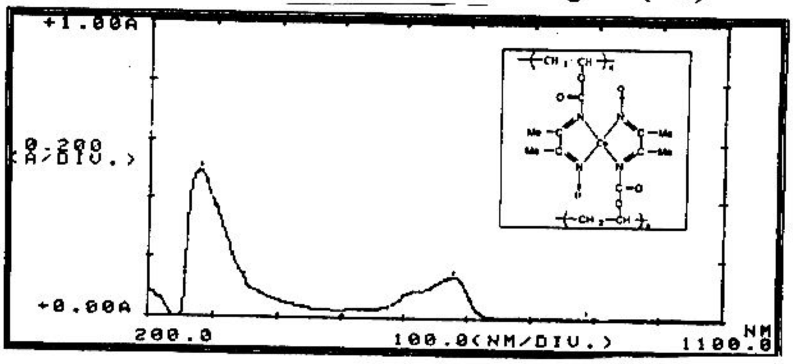


Figure (3a) The U.V-Vis spectrum of the complex $[Co(L)_2]X$.

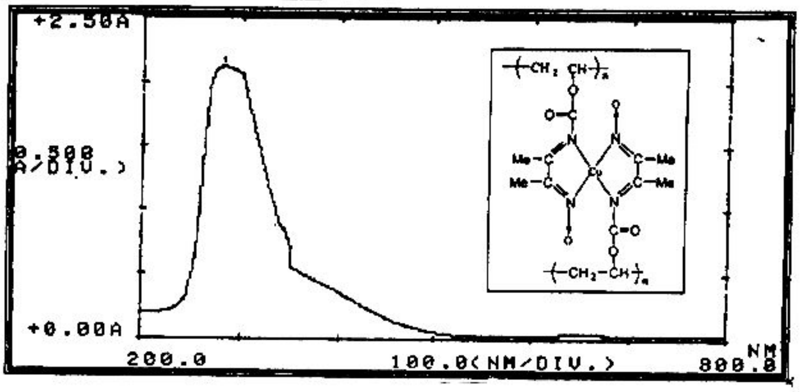


Figure (3b) The U.V-Vis spectrum of the complex $[Cu(L)_2]X$.

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية المجلد21 (2) 2008

تحضير معقدات البولي فنيل يورثنايز اوكزيم لأيونات Hg(II),Cu(II),Co(II) ودراستها طيفيا

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الخلاصة

تضمن البحث تحضير الليكاند البوليميري الجديد نوع (امين- اوكسيم) ثنائي السن (N_2) ذي الصيغة [HL].وذالك من مفاعلة (Poly Vinyl Alcohol) مع ال (Urea) ثم مفاعلة ناتج هذه الخطوة مع (ثنائي استيل الاوكزيم). كذالك حضرت معقدات هذه الليكاند من مفاعلته مع املاح بعض العناصر (الكوبلت ، النحاسوالزئبق) التي لها الصيغة العامة $[M(L)_2]X$ ، اذ M=Co,Cu,Hg, $X=H_2O$

شخصت جميع المركبات المحضرة بالطرائق الطيفية الاتية (الاشعة تحت الحمراء والاشعة فوق البنفسجية–المرئية–ومطيافية الامتصاص الذري).

كذالك شخصت بوساطة التحليل الكمي الدقيق للعناصر مع التوصيلية المولارية الكهربائية. ومن النتائج اعلاه الشكل الفراغي المتوقع لمعقدات Co,Cu,Hgهو رباعي السطوح المشوه