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Preparation and study of some Transition Metal Complexes with Liquid Crystal Properties

Omar Hamad Shehab

University of Anbar - Women Education College

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ABSTRACT

Acetylenic amine (N,N-Bis propargy piperazine) were synthesized and diagnosed in spectroscopic method (Uv-visibl and IR) and (C.H.N) analysis. Preparing and studying new complexes by using ligand that from acetylenic amine which using this purpose at the first time with metal chlorides (Mo+3, Cr+5,W+6, Fe+3). Studying of complexes by using suitable methods have been diagnosed in Uv-Visible, IR, Magnetic susceptibility , atomic absorption ,electric conductivity measurement and molar ratio, all result obtained from different techniques above which were found that their corresponding with the proposed structures for the prepared complexes . Complexes appeared liquid crystal properties therefore they have been studied careful (ΔH, ΔS) of liquid crystal stages for both changes calculated which were found that their corresponding with the data in literature.

Introduction:

Acetylenic amines are important class of compounds due their pharmacological properties such as activity, low toxicity and easy absorption by the body. Moreover these compounds are electron rich and easy to bond with receptor proteins(1). Some of their pharmaceutical uses as anticancer (2) and hypertensive agent(3).

In investigating the importance of acetylenic bond for pharmacological activity it was though possible that the electron rich acetylenic bond attaches itself to the positive binding site in the cholinergic receptor, in which case its presence is probably necessary for the effect. it is also possible that the rigidity of the system serves the purpose of keeping the two nitrogen atoms at suitable distance from each other.

The acetylenic amines derived from piperazine having two acetylenic functions are expected to have similar anticolinegic effect and may be used to treat Parkinson disease.

The first stable acetylenic complexe were reported by Gelman (4) who showed that the acetylenic glycol, forms complexes such as trans-[PtCl2(ac)Py] analogous to trans-[PtCl2(C2H4)Py] (5). Later work (6) showed that Olifine complexes of the types K[PtCl3(ac)], alkyne Pt+2 complexes (7) of the chloro bridge type [Pt2Cl4(ac)] and M[Pt2Cl3(ac)] (M=Na,K).

A large number of compounds have been prepared specially those having aromatic rings substitute in 1,4-positions to have crystals with rigid and linear structures. In addition a number of compounds with piperazine ring (8) and acetylenic group (9) were prepared and found to liquid crystalline properties.

Also, a large number of metal complexes shows liquid crystal properties with central atom like Pt, Ni and Fe (10,11).

The wide range of application of the ligand and its metal complexes a roused our interest to prepare some of these metal complexes.

Experimental:

Instrumentation:

IR spectra were recorded on a PYE-UNICAM SP3-100 and samples used as KBr disc. UV-VIS data were recorded on a HITACHI-U-2000 and Melting point determined by Gallen Kamp. Electrical conductance was measured at (10-3-10-4) M on conductivity CDC304 (JENWEY 4070). Metal contained were done by Atomic absorption AA-680G Shimadzu, Polarizing Microscope Labrotux (2-po) Letizand Camera Orthomato 25 Letiz, Magnetic susceptibility B.M6 Bruker.

Material:

All the chemical used were of analar grade, and purchased from Sigma-Aldrich. Metal salts were

* Corresponding author at: University of Anbar - Women Education College, Iraq.E-mail address: scianb@yahoo.com

purchased from Fluka AG Buchs. All the solvents used were of spectroscopic grade.

Preparation of the ligand:

The ligand (N,N-Bis propargel piperazine) (L) was prepared according to literature method(12), it was pale yellow crystals in 64% yield, m.p.100-102 oC. The IR spectrum showed the characteristic peaks: υC≡C 2100 cm-1, υ≡C-H 3290 cm-1, υC-H 2960 cm-1. The UV spectrum in DMSO showed the following characteristic bands 319 nm, 372 nm. Anal. Calcd. For (C16H16N4O7) (L): C,51.06; H, 4.25; N,14.89 .Found: C,51.04 ; H, 4.21 ; N,14.85

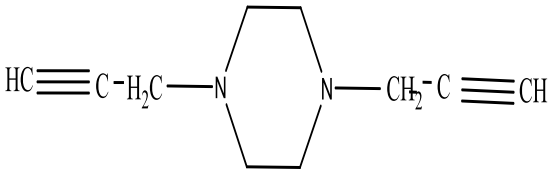

Fig.1: structure of Ligand (L)

General procedure for preparation of complexes:

All complexes were prepared by the following methods; A solution of the ligand (2 mmole/l) in absolute ethanol were prepared and reacted with various metal chlorides in the required molar ratio.

To a solution of (L) (2 mmole/l) in absolute ethanol ,a hot ethanolic solution (96%) containing (2 mmole/l) of (Mo+3,Cr+5,W+6,Fe+3) was gradually added with stirring the product .the colour of the resultant mixture changed immediately , the mixture was left over night . a colored solid precipitate was separated and colleted by filtration under vacuo, then it was washed successively with ethanol and recrystallized from absolute ethanol/ether (1:1) to give colored complexes .

Analogous complexes were prepared in a similar manner to that described above by adding a hot solution of the same metal chloride above (2 mmole/l) to a solution of ligand (1 mmole/l). The complexes are listed in table(1).

RESULT AND DISCUSION:

IR Spectra

The spectra of all prepared complexes were prepared with ligand spectra in the region (4000-200) cm-1. Stretching vibration of (C≡C) bonds for the prepared ligand appear near (2100) cm-1 (13). This peak will shifted to lower frequency by (490) cm-1 (i.e. to 1750-1650) cm-1 the peak which belong to the frequency (C≡C) disappeared producing the change in ligand peak shape and appear intensity more than complex as shown in table(1). υM-N frequency appears in the region (315-345) cm-1 which indicating the involving of nitrogen atoms in coordination with metallic ion.

Electronic Spectra

UV-Visible spectra for the prepared ligand show two bands, the first band at (319) nm and the second at (372) nm as shown in table (1).comparing the UV-Vis for free ligand solution with metal complexes ,clear sudden change have been made in bands spots wether increasing or decreasing in wavelength or by new absorbance band for all preparation complex which belong coordination complex formation ,the change in color wee occurred after mix ligands solution with metal salt, the mixtures color differ fee ligand and metal salt colors indicate occurring complexation , the data in table (1) clearly show that that bands in all complexes appear shifted in λmax, compared to the same bands in the free ligand signs this band is due to (π-π*) and(n-π*) and this shifted in λmax can be to indicate the complexation between ligand and metal ions(14).

Magnetic Study

From table(1) the magnetic susceptibility were experimentally measured for (Fe+3 and Cr+3) complexes were correspondences with theoretical data for its complexes (coordination number six) with octahedral structure(15).

Molar Conductance

The measurements of the molar electrical conductivity of the complexes in DMSO solvent are prepared in table (1). The results clearly show the values for the molar conductivity of the complexes of metal ions and are non-electrolyte whereas the high values of the molar conductivity show that these complexes are electrolyte.

Stochiometric Study

Molar ratio (2:2) ligand to metal (M2L2) was also obtained for the complexes by molar-ratio method as shown in fig.(2a), another molar ratio (1:2) of ligand to metal (M2L) is effected by the absorption due to change in the coordination metal ion of the ligand complexes as shown in fig.(2b) by continues variation method.

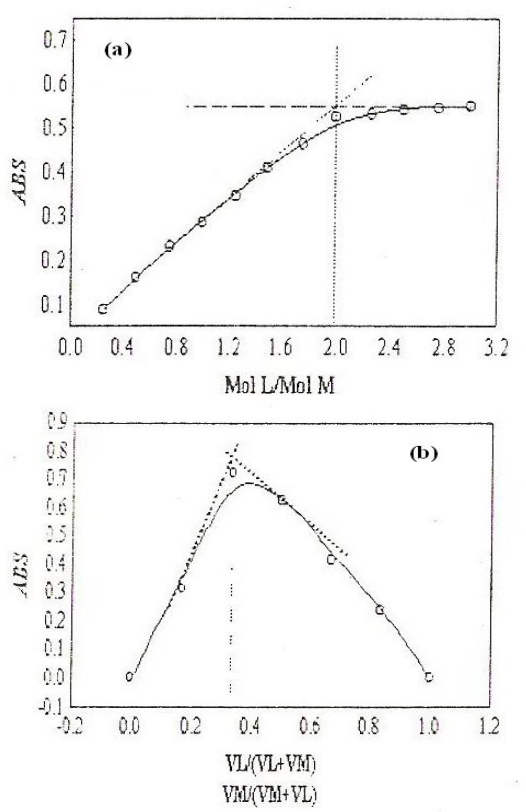

Fig.(2a,b): Molar-ratio curve for some of prepared complexes

According to the results obtained from ir, uv/vis, molar ratio, molar conductivity and atomic absorption measurements for the prepared complexes, the proposed molecular structure of the complexes has an octahedral structure as shown below fig. (3).

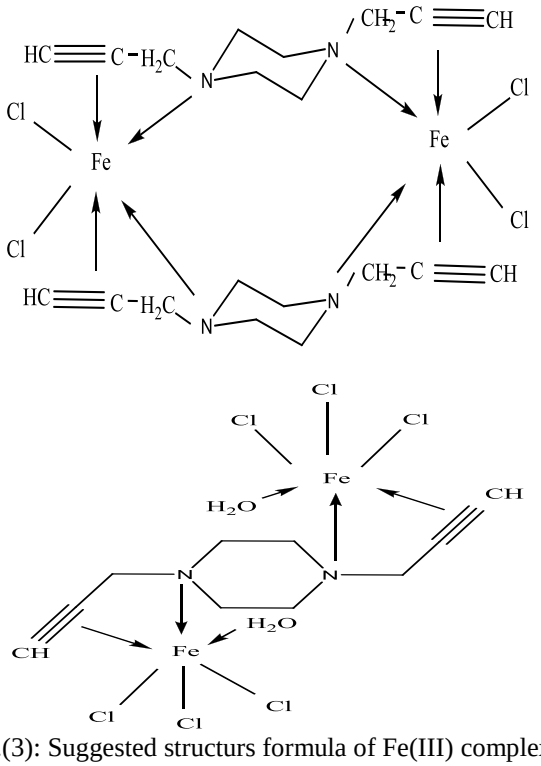

Fig.(3): Suggested structurs formula of Fe(III) complexes

Liguid- Crystal Study

Liquid-crystal properties of the prepared complexes have been studied by using (DSC) with polarized microscope, which proved a tool to determined temperatures transition from crystal phases to the liquid crystal phases then converted to the isotopic liquid phase , these transitions are denoted as (TC-LC) (TLC-L) . it is possible also using same technique to calculate the changes in enthalpy and entropy of transitions for compound phases. Te polarized light microscopy provides the changes in the liquid crystal phases, and transition temperature and comparing these data with (DSC) method.

ΔH and ΔS values for transition of the prepared complexes, calculated by DSC and summarized in table (2), the prepared complexes gave two transitional peaks, the fist represents peak for any transitional from solid crystal phase to the nematic phase according to the isotopic liquid phase, so the order peak represent the transition to the isotropic liquid phase , so the ideal linear texture for nematic liquid crystal phase, this contributed to the highly polarized phase for terminal acetylene group which increase the effectiveness.

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Table (1): physical properties for prepared ligands and their transition metal complexes

No.	Complexes	Color	ΔM/ s cm^2 mol^{-1}	UV-Vis. (nm)	Elemental Analysis %Cal.(%Found)		IR Spectra cm^{-1}			μeff (B.M)
					M	Cl	υC=C	υ≡C-H	υM-N	
١	$[Cr_2(L)(H_2O)_2Cl_6]$	Green	15	303,373,620	20,15(20,10)	40.69(40.63)	1700	3300	335	٣.75
2.	$[Cr_2(L)_2Cl_4]Cl_2$	Green	60	302,389,630	16.09(16.0)	32.5(32.41)	1705	3300	340	3.70
3.	$[Mo_2(L)Cl_8]Cl_2$	Blue	65	295,383,467	27.19(27.11)	49.57(49.49)	1650	3300	335	-
4.	$[Mo_2(L)_2Cl_4]Cl_6$	Blue	150	299,373,465	22.01(21.97)	40.13(40.06)	1655	3300	315	-
5.	$[W_2(L)Cl_8]Cl_4$	Yellowish green	120	325,370,421	30.13(30.6)	57.22(57.16)	1670	3300	325	-
6.	$[W_2(L)_2Cl_4]Cl_8$	Yellowish green	190	296,398,430	20.44(20.39)	46.66(46.58)	1660	3300	330	-
7.	$[Fe_2(L)(H_2O)_2Cl_6]$	Brown	20	304,387,438	21.45(21.39)	4.22(4.18)	1680	3300	320	5.69
8.	$[Fe_2(L)_2Cl_4]Cl_2$	Brown	70	313,373,425	16.27(16.21)	30.52(30.48)	1670	3300	325	5.77

Table (2): ΔH and ΔS values for prepared transition metal complexes

No.	Kind of Transition	T °C	T K	ΔH (J/gm)	ΔH (J/mole)	ΔS (J/mole K)
1.	C-N	60	333	30.38	15.68	47.08
	N-I	120	393	31.10	16.05	40.83
2.	C-N	70	263	11.95	18.5	45.33
	N-I	140	412	29.24	19.01	71.23
3.	C-N	36	309	27.88	19.69	64.13
	N-I	125	393	28.79	20.33	51.08
4.	C-N	70	343	26.68	23.27	67.84
	N-I	138	411	27.54	24.02	58.44
5.	C-N	35	308	23.06	20.76	67.4
	N-I	115	388	23.29	25.88	66.7
6.	C-N	120	393	25.49	22.86	58.16
	N-I	200	473	26.88	24.2	51.16
7.	C-N	50	323	51.78	27.01	83.62
	N-I	188	461	58.06	30.13	65.35
8.	C-N	55	328	45.13	31.05	94.6
	N-I	175	448	50.59	34.81	77.7

تحضير ودراسة بعض معقدات العناصر الانتقالية ذات الخواص البلورية السائلة

عمر حمد شهاب

E.mail: scianb@yahoo.com

الخلاصة:

تم تحضير الأمين الاستليني (N,N-Bis propargyl piperazine) وشخص المركب بالطرق الطيفية الأشعة فوق البنفسجية والمرئية والأشعة تحت الحمراء إضافة إلى التحليل الدقيق للعناصر (C.H.N). تم تحضير ودراسة معقدات جديدة تحضر لأول مرة باستخدام الأمين الاستليني المحضر كليكند مع أملاح العناصر الانتقالية (Mo+3, Cr+5, W+6, Fe+3). تم تشخيص المعقدات المحضرة بالطرق الطيفية المناسبة وهي الأشعة فوق البنفسجية – المرئية، الأشعة تحت الحمراء، الحساسية المغناطيسية، الامتصاص الذري، قياسات التوصيلية الكهربائية، والنسب المولارية وقد أيدت النتائج المستحصلة من مختلف التقنيات التراكيب المقترحة للمعقدات المحضرة. أظهرت المعقدات المحضرة صفات بلورية سائلة لذا فقد درست تفصيليا وتم حساب الدوال الثرموديناميكية (ΔH, ΔS) للأطوار البلورية السائلة والتي وجد أنها تتطابق مع القيم المنشورة في الأدبيات في هذا المجال.