Preparation and Characterization of Cr (III), Mo (V), and W (VI) Complexes Using Some Schiff Bases

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PREPARATION AND CHARACTERIZATION OF CR (III), MO (V) AND W (VI) COMPLEXES USING SOME SCHIFF BASES

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Abstract:

This research consists of the synthesis of two Schiff base ligands whose name are as follow: phenyl -3- methyl -5- pyrazolone thiosemicarbazone = (L1) and Phenyl -3- methyl -5- pyrazolone-4- phenyl thiosemicarbazon = (L2) The complexation of the above ligands with some transition metal ions (Cr (III), Mo(V), W(VI)) afforded metal complexes which have been characterized on the basis of their (C.H.N) elemental analysis, IR, UV-VIS, and atomic absorption. The molar conductivity measurement and melting point of prepared complexes were measured to investigate the proposed structure as an octahedral.

Key words: Preparation . characterization . Cr (III), Mo (V) . W (VI) . Schiff bases

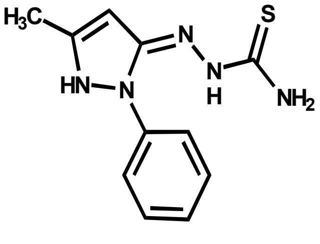
Introduction:

The complexes of Schiff base and their derivatives have useful and importance applications, as well as, biological activities have taken a keen interest in medicine and a significant correlation between the chelating properties and anti tumor activity or various disease because it is known that some drugs have increase activity when administered as metal complexes and a number of metal chelates inhibit tumor growth (1).

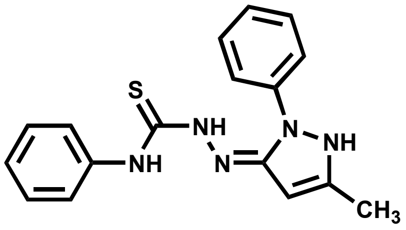
The thiosemicarbazide and thiosemicarbazones have attached special attention due to their activity against viruses prato zoa, small pox and certain kinds of tumor (2,3), it is known that some drugs have increased activity when administrated as metal complexes (4,5) and a number of metal chelates inhibit tumor growth (6). For many years thiosemicarbazide has been known to form complexes with certain transition metal ions and most of this work has been reported by Jensen (7).

Extended studies of the investigation of metal complexes of thiosemicarbazone have been given in table (8). Complexes of Schiff bases with metals have not been prepared except in Ziad (9) was prepared some of this complexes by reaction these ligands with metal chloride, acetate, sulphate and nitrite some transition elements.

We have, therefore, undertaken a synthetic and structural study of the above new type of complexes metal (Cr (III), Mo (V), W (VI); bidentate ligands these:



1-phenyl -3- methyl -5- pyrazolone thiosemicarbazone = (L1)



1-Phenyl -3- methyl -5- pyrazolone-4- phenyl thiosemicarbazone = (L2)

EXPERMENYAL:

INSTRUMENTATION:

Apye – Unicam sp3-100 infrared spectrophotometer was used to record the ir spectra as KBr disc and CsI disc , UV/VIS spectra were measured by a HITACHI U-2000 spectrophotometer, Elemental Analysis were done by atomic absorption AA-680G (Shimadzu). The elemental analysis (C.H.N) founded on (Carlo Erba micro analyzer type 1106).Electrical conductance was measured on conductivity CDC304 (Jenway4070) in DMSO solvent at (10-3M), Melting points were determined by an electric heated block apparatus (Gallen Kamp), and were uncorrected.

MATERIALS:

The hydrated metal chlorides [CrCl3.6H2O] , [MoCl5.6H2O] , [WCl6.6H2O] were supplied by BDH chemicals, ethanol absolute , diethyl ether, dimethyl sulfoxide , 4-phenyl thiosemicarbazide, 1-phenyl-3-methyl-5-pyrazolone and thiosemicarbazide supplied by Aldrich .

A- Preparation of (L_1), (L_2) was prepared according to the literature [10] as shown bellow:

Preparation of (1-phenyl-3-methyl-5-pyrazolone thiosemicarbazide) (L1): To a hot solution of (1-phenyl-3-methyl-5-pyrazolone) (1.91 gm, 0.011 mole) in absolute ethanol (15 ml) a hot solution of (Thiosemicarbazide) (1 gm, 0.011 mole) in absolute ethanol (15 ml) was added. The resulting mixture was then refluxed for 6 hours, during which time a yellow precipitate formed then was cooled, lifted overnight at room temperature. This was collected by filtration in vacuo, washed and recrystallized from absolute ethanol/ether to give a yellow needle shaped crystalline solid.

Preparation of (1-phynyl-3-methyl-5-pyrazolone 4- phenyl thiosemicarbazide) (L_2):

To a hot solution of (1-phynyl-3-methyl-5-pyrazolone) (2.083 gm, 0.012mole) in absolute ethanol (10 ml) a hot solution of (4- phenyl thiosemicarbazide) (2 gm, 0.012 mole) in absolute ethanol (10 ml) was added. The resulting mixture was then refluxed for 6 hours, during which time the solution became bright yellow in colour, then was cooled, lifted overnight at room temperature, after this time a yellow precipitate formed. This was collected by filtration in vacuo, washed and recrystallized from absolute ethanol/ether to give a white crystalline solid.

The full name of the Schiff base will be replaced by the symbols (L1, L2) respectively as shown in table (1) for the rest of this paper. The physical properties of these compounds (L1, L2) are listed in table (1). The characters ir bands and uv/vis spectrum in DMSO as shown in table (2), (3).

B- General procedure for preparation of metal complexes :

To a hot solution of ligands (L1 or L2) (2 mmole) in absolute ethanol (5 ml), a hot solution of metal chloride (1 m mole) in absolute ethanol (5 ml) (dissolved in dilute HCl) [11] was added and the resultant mixture was stirred and refluxed for 2 hours, the color of the solution changed immediately, the reaction mixture was cooled, and the solution was evaporated in vacuum, or left over night at room temperature , then precipitate formed, collected by filtration in vacuo, washed and recrystallized from absolute ethanol/ether.

The physical properties of prepared complexes are listed in table (4). The analogous complexes were prepared in a

similar manner to that described above by adding a hot solution of (1 mmole) in absolute ethanol (5 ml) to a hot solution of metal chloride (1 mmole) in absolute ethanol (5ml).The molar ratio of the complexes was determined according to the methods (12).

RESULTS AND DISCUSSION:

The structures of Schiff base complexes were confirmed by spectroscopic techniques like ir and uv /visible. The infrared spectra of the two ligands (L1),(L2) show the usual broad bands in the region around (3400-3350 cm-1) and (3360-3475 cm-1) respectively due to the NH and NH2 stretching frequency (13) of the amide groups of the ligand , practically no effect on these frequencies after complexation precludes the possibility of complexation at this group (10).

The band at 1640 cm-1 in the spectrum of (L1) due to symmetrical C=N stretching decreased in the complexes, while the band at 1620 cm-1 was assigned to asymmetrical C=N frequency, which shifted to the lower frequencies in the complexes (14) (table 4), the C=N stretching frequency of the (L2) observed at 1625 cm-1 shifted to 1600-1620 cm-1 in the complexes (15) (table 4). The negative shift generally in C=N further suggested the coordination to metal ions through nitrogen atom of (-C=N-) Schiff's base (16,17) of the ligand and on complexation indicates involvement of azomethine nitrogen (6, 11, 13, 14, 18) with metal ions.

The band at 825 cm-1 in the spectrum of (L1) due to C=S stretching vibrations. In the metal complexes this band is weakened and lowered (19) (table 4). The C=S stretching vibrations of the (L2) contributed two bands at 1280 cm-1 and 895 cm-1 (20). Also in the metal complexes these bands are weaked and lowered (table 4), the observations indicate the coordination of the ligands through sulphur atom.

New bands were appeared at low frequencies region in the spectra of the prepared complexes were probably due to (metal- nitrogen), (metal- sulpher), and (metal- chloride), vibration frequencies (table 4). The complexes give different colour from the transition metal salts and the ligands, then this was important indication to coordinate occurrence (21,22), therefore these colourly complexes show different characteristic absorption band , intensity or together when compared with the bands of ligand and this was another indication for the coordination occurrence (23,24). The uv/visible spectra of the two prepared ligands (L1, L2) at (10-3M) in ethanol were showed two absorption bands (25). The first band between (245-259) nm represented (π- π *) while the second band (308-310) nm represented (π- π *) transition and called (B-band) for phenyl group (24, 25). Generally in the new prepared complexes these bands are shifted to short or long wavelength compared with free ligands and high intensity of the bands is indicate for complexes formation (23,24) are shown in table (4).

The measurements of the molar electrical conductivity of the complexes at (10-3M) at (25°C) in di methyl sulphoxide are presented in table (4). These results show the high values of the molar conductivity, these complexes are electrolyte and low values refer to the complexes are non-electrolyte, are in agreement with the proposed structures of the complexes (26).

The continuous variation method to evaluate the mole ratio (M: L) were employed in this work, the molar ratio (1:2) metal to ligand for (1-6) complexes and (1:1) metal to ligand for (7-12) complexes.

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

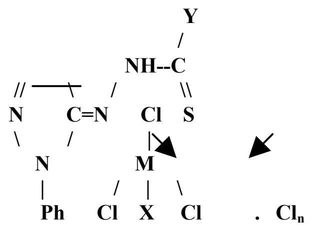
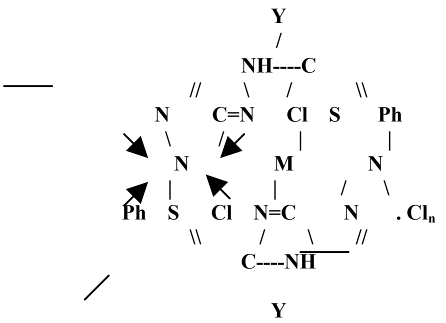
	
Y:[$(L_1)=NH_2$, $(L_2)=NHPh$] **Complex no. (7,10) :- ($M=Cr,X=H_2O,n=0$)** **Complex no. (8,11) :- ($M=Mo,X=Cl,n=1$)** **Complex no. (9,12) :- ($M=W,X=Cl,n=2$)**	**Y:[$(L_1)=NH_2$, $(L_2)=NHPh$]** **Complex no. (1,4) :- ($M=Cr,n=1$)** **Complex no. (2,5) :- ($M=Mo,n=3$)** **Complex no. (3,6) :- ($M=W,n=4$)**

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Table (1): physical properties of the Schiff base ligands

No.	Yield %	M.P C°	Elemental analysis (% cal.) % found			colour
			C	H	N	
L_1	85%	174-176	52.98 (53.42)	5.37 (5.30)	28.24 (28.32)	Yellow
L_2	87%	134-136	62.87 (63.14)	5.40 (5.30)	21.45 (21.65)	white

Table (2): The characteristic ir bands of the Schiff base ligands

No.	C=N sy. Str. cm^{-1}	C=N asy. Str. cm^{-1}	C=S sy. Str. cm^{-1}
L_1	1640 vs.	1620 vs.	825 bm
L_2	1625 vs.	-	1280 m , 895 m

Sy=symmetrical, asy= asymmetrical, vs. = very sharp, medium, bm=broad medium,

Table (3): UV-VISIBAL absorption of the Schiff base ligands

No.	π- π *	π- π *
L_1	249 nm	308 nm
L_2	246 nm	310 nm

Table (4): some physical and chemical properties of the prepared complexes

No.	complexes	Colour	ΔM#	M.P C°	UV/VIS nm	Elemental analysis		IR SPECTRA cm^{-1}					
						(% found)% cal							
						M%	Cl%	C=N sy Str.	C=N sy Str.	C=S Str.	M-N Str.	M-S Str.	M-X Str.
1	$[Cr(L_1)_2Cl_2]Cl$	DG	65	185-187	294,310,595	8.3	17.25	1620 bs	1595	800 bm	460 bm	390 bw	270 w
2	$[Mo(L_1)_2Cl_2]Cl_3$	B	80	205-207	252,310,495	12.93	24.25	1615s	1590	795 bw	475 bm	385 w	290 m
3	$[W(L_1)_2Cl_2]Cl_4$	DG	88	211-213	284,308,530	21.15	24.97	1625 m	1600	790 bm	465 bs	365 m	310 bw
4	$[Cr(L_2)_2Cl_2]Cl$	DG	67	190-193	248,314,605	6.68	13.88	-	1610	1250, 870	480 bw	385 bm	250 bm
5	$[Mo(L_2)_2Cl_2]Cl_3$	B	85	208-210	250,315,501	10.73	20.13	-	1600	1260, 850	470 bm	373 bs	235 m
6	$[W(L_2)_2Cl_2]Cl_4$	DG	90	210-213	249,313,545	18.07	21.21	-	1605	1270, 860	450 bm	380 w	215 w
7	$[Cr(L_1)Cl_3H_2O]$	DG	15	188-190	250,309,590	12.65	26.27	1625 ms	1590	790 m	450 bs	380 m	260
8	$[Mo(L_1)Cl_4]Cl$	B	58	209-211	251,311,490	18.86	35.36	1630 bm	1585	802 bm	470 m	375 m	285
9	$[W(L_1)Cl_4]Cl_2$	DG	65	218-220	249,310,520	29.06	34.12	1615	1595	795	460	370	300
10	$[Cr(L_2)Cl_3H_2O]$	DG	15	195-197	247,312,587	10.67	22.17	-	1605	1255, 865	475	390	242
11	$[Mo(L_2)Cl_4]Cl$	B	56	215-217	249,311,485	16.41	30.76	-	1615	1265, 855	460	365	225
12	$[W(L_2)Cl_4]Cl_2$	DG	60	230-232	250,312,510	25.95	30.46	-	1600	1275, 875	455	380	230

تحضير وتوصيف معقدات Cr (III), Mo (V) and W (VI) باستعمال بعض قواعد شف

عبد الهادي رجب حبيب الهيتي عمر حمد شهاب العبيدي
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الخلاصة:

يتضمن البحث تحضير معقدات اثنين من قواعد شف(كليكندات) التي لها الاسمين الآتيين:
1- فنيل -3-مثيل-5- بايروزولون ثايوسيميكاربزون =(L1) و فنيل -3-مثيل-5- بايروزولون -4- فنيل ثايوسيميكاربزون =(L2) حيث تم تحضير معقدات لهذين الليكندين مع بعض أملاح العناصر الانتقالية التي تشمل ((Cr(III) ,Mo(V) W(VI)) وقد تم تشخيص ودراسة تراكيب الليكندات والمعقدات المحضرة منهما باستخدام تقنية التحليل الدقيق للعناصر (C.H.N) ومطيافية الأشعة تحت الحمراء والأشعة فوق البنفسجية وتقنية الامتصاص الذري إضافة إلى قياس الموصلية الكهربائية المولارية ودرجات الانصهار للمعقدات المحضرة وعلى ضوء النتائج تم التحقق من تراكيب هذه المعقدات بشكل ثماني السطوح.