Synthesis and Structural Study of Some Mo(II) Carbonyl Complexes with Triazole and Oxadiazole Derivatives

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Abstract

A new carbonyl complexes of triazole and oxadiazole were synthesized. These complexes were identified and their structural geometric were suggested by using FT-IR and UV-Vis spectra, conductivity measurements and other chemical and physical properties.

The spectra data (FT-IR, UV, Vis.) with the substantial aid of group theoretical calculations gave so many evidences for the proposed geometries and the type of bonding of these compounds

Introduction

Transition metal carbonyl complexes are the basic starting materials for the synthesis of many organometallic compounds, which are mainly used as catalysts for the reactions of unsaturated hydrocarbonates[1-4].

Heterocycles and in particular the five-membered rings e.g. mercapto derivatives of triazole and oxadiazole have received more attention during the last decades as bioactive moieties and of industrial application of these rings [5-7]. Also,they were included in many basic structures of drugs and important ones of octane numbers [8].

Further, the triazole and oxadiazole derivatives were suggested that (-SH) group attached to heterocyclic nucleus may induce fungicidal activity [9,10].

The interaction of these rings with metal carbonyl complex gives a great interest for versatility and diversity form the point of structural, biological and catalytically espects. Also, beside their useful application, they have the effect on the coordination nature of the resulted ones, especially the olefinic group in the triazole structure is a good coordinating moiety may link to number of metal ions forming organometallic compounds structure [11]. Also, subsequently nature of bands and numbers of CO group were attached to metal [12,13].

Hence, the present work investigated the reaction of the three ligands from the Bis - triazole and Bis-oxadiazole derivatives with carbonyl groups $Mo(CO)_4bipy$ was prepared from the reaction of 2,2'-bipyridly with $Mo(CO)_6$ under in an atmosphere of nitrogen to formaly a new carbonyl complexes.

According, the characterization of these complexes would be presented and the results would be discussed with spectroscopic investigation, physical techniques group theoretical calculations.

Experimental

Materials

All chemicals used were of highest purity available.

Physical Measurements

Melting points were recorded uncorrected of Stuart melting point apparatus. FT-IR spectra were obtained by using Shimadzu FT-IR-8400 Spectrophotometer in the rang (4000-

200) cm^{-1}, U.V-Vis spectra were recorded by using Shimadzu UV-160A Spectrophotometer in $CHCl_3$ solvent in the rang (200-700) nm.

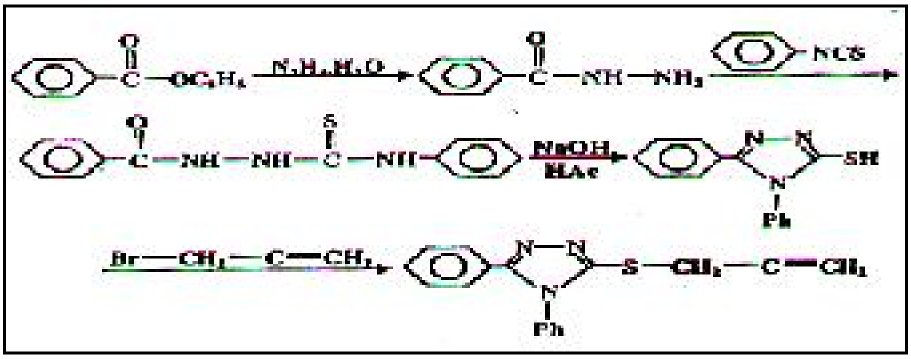
Conductivity measurements were obtained by PW 9525 digital conductivity meter.

Preparation of Compounds

Preparation of the ligands

1- Preparation of (OTRZ) [4,5diphenyl-3(2-propynyl) thio1,2,4-triazole].

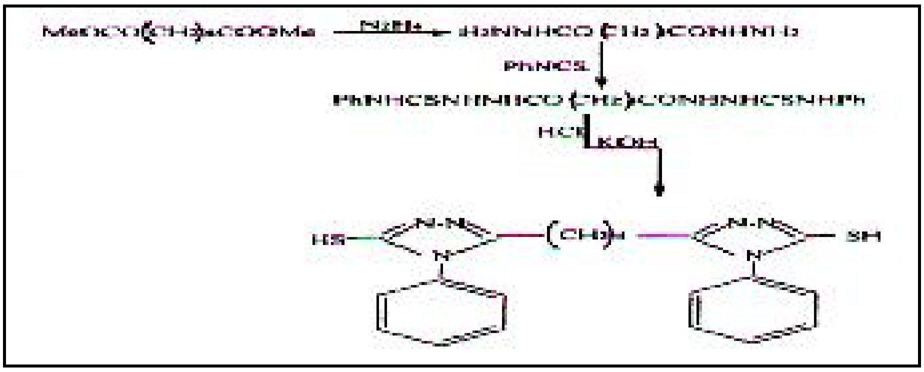
(OTRZ) was prepared from ethyl benzoate as according to the literature method [11] and as shown by scheme (1).



Scheme (1)

2- Preparation of (TRZ) [bis(4-phenyl-3-thiol-1,2,4-trizaole 5yl)butane].

(TRZ) was prepared following general procedures decribed in the literature [14] as shown in scheme (2).



Scheme (2)

3- Preparation of (OXZ) [bis(3-thiol-1,3,4-oxadiazole-5yl) butane].

(OXZ) was prepared by a modified literature method [15] and as shown in scheme (3).

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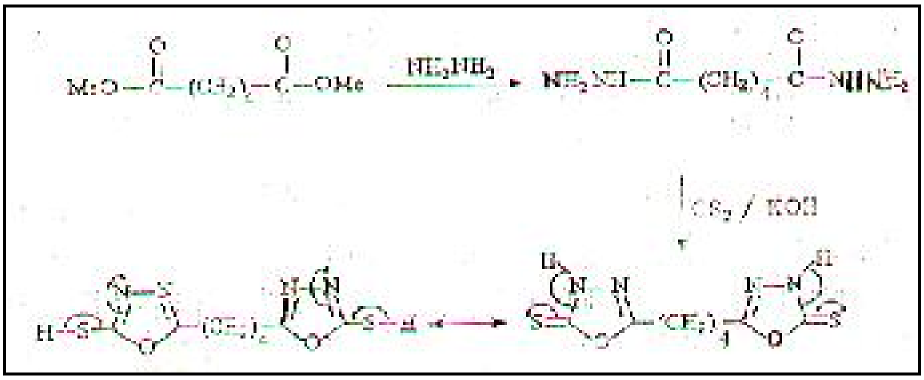

Scheme (3)

Preparation of the Metal Carbonyl Complex [Mo $(CO)_4$ bipy] (M)

Tetra carbonyl mono -2,2'-bipyridyl molybdenum (O) was prepared according to the literature method [16].

The mixture of $Mo(CO)_4$ (53mmole, 1.4g) and bipyridyl (5.12mmole,0.8g) were refluxed in toluene (50ml) for 1.5hr under N_2. After cooling, the red crystalline complex was washed with a mixture of toluene, (15ml) and light petroleum (30ml) and dried under vacuum.

The product was stable toward air and moisture, soluble in polar solvents but insoluble in petroleum spirit and water.

Preparation of the Mixed Ligand Carbonyl Complexes. [Mo^{II} $(CO)_3$ bipy (OTRZ)]I_2 (MI), [Mo^{II} $(CO)_3$ bipy (TRZ)]I (MII) and [$Mo^{II}(CO)_3$bipy (OXZ)]I (MIII)

These complexes were prepared by dissolving $Mo(CO)_6$bipy (0.16mmole) in chloroform (50ml) then treated with iodine (0.40mmole,0.1g) in (25ml) chloroform with stirring at OC°, the bright orange mixtures were obtained. (OTRZ) (0.32mmol,0.09) and (TRZ) (0.32mmol,0.13g)dissolved in (10ml) chloroform while, the (OXZ) (0.32mmole,0.09g) dissolved in (1:1) ml of a (chloroform /ethanol) mixture were added drop wise, stirring at OC° for 6hr., then the solvent was slowly evaporated to obtain nicely colored crystals.

These complexes are stable in air, have high melting points as shown in table (1) and soluble in DMF and $CHCl_3$ solvents but insoluble in water.

The complexes were indentified by spectral (FT-IR and U.V) and physical methods. Table (1,2).

Results and Discussion

Spectroscopic Characterization of New Complexes

Vibrational Spectra

The characteristic (FT-IR) bands observed and the vibrationl assignment of the ligands and their metal complexes are explained in detail in tabled (2).

The spectrum of (OTRZ) is characterized by the presence of an essential band which belongs to the olefinic group at ($1630cm^{-1}$) and other bands at (965 & 885 cm^{-1}) which was originated out of the plane bending vibration of the vinylic group, where the spectrum of the complex (MI) shows red shifts of the olefinic band absorption to ($1550um^{-1}$) and to ($925\&832cm^{-1}$) for the vinylic CH_2 group, which indicate π -bonding between the metal and olefinic group [17], this was further indicated by the appearance of (Mo-C) band absorption, table (2).

A comparison of the IR spectrum of the ligands (TRZ and OXZ) and their complexes leads to the medium -SH band of the ligands at ($2530\&\ 2560cm^{-1}$) respectively, which disappear indicating the displacement of hydrogen SH by means of metal ion.

The γC=N+C=S band of the (TRZ) at ($1270cm^{-1}$) is splitted on coordination at ($1310\&1253\ cm^{-1}$) while , the (OXZ) showed two distinct peaks,the first one at($1315cm^{-1}$) and the second at (1250 cm^{-1}) red shift in complex to (1570 cm^{-1}) which could be attributed to C=N stretching . This account for the C=N and sulphur that coordinated to the metal ion [18-21].

The appearance of new bands in the IR spectra of these complexes in table (2) is propably due to the formation of (M-C), (M-N) and (M-S) developed through complexation (21) .

IR Spectra for Carbonyl Groups of (MI, MII and MIII) and Their Group Theoretical Calculations

The compound studied in the present work is of the formula [Mo $(CO)_4$ bipy] , where (M) is bipy either monodentate or bidentate nitrogen donor. Hence, the bidentate ligand must belong to the C_{2v} group [12,22],while the geometrical isomer is shown in scheme (4).

Theoretically ,the cis-isomer should give four IR bands, the spectra of the prepared (M),showed four principle bands in the region(2000-1825)cm^{-1} in table(2), fig(1), which can be assigned to terminal γ CO virbrations.

The presence of four bands indicated cis- isomeration. for the bidentate bipy complex .

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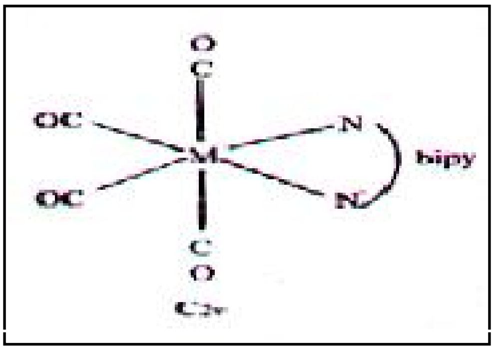
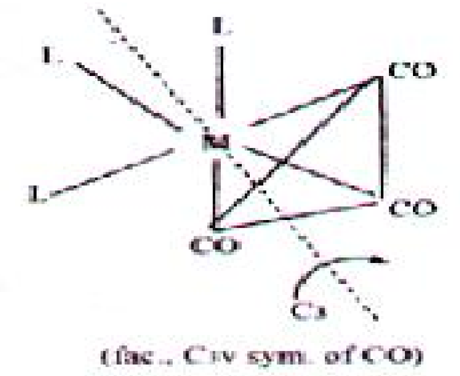


Scheme (4)

First of all, it was found that the CO spectral band position for Mo complexes, showed that all the CO groups to be terminal, no bridging CO exist in fig (2).

The prepared complexes are contain three Carbonyl groups which may have facial configurations.

The point group for the molecules is Cs,while the point group considering for CO moieties is C_{3v} for facial configuration and the main axis of symmetry is shown in scheme (5).



Scheme (5)

According to the group theoretical calculations based on C_{3v} point groups, the number of CO vibration modes were calculated and the results are shown in table (3).

The CO stretch of the E mode (C_{3v}) splits A' and A'' compounds characteristic of the overall molecular symmetry of Cs, this was the case for the complex (MI), i.e. three carbonyl bands, due to 2A',/A''modes were found .

The other complexes show only two bands as in the case of compounds (MII, MIII), this is because the two close-lying bands due to A +E modes were observed. Generally the E mode is the lower frequency band [23,24].

Electronic Spectra

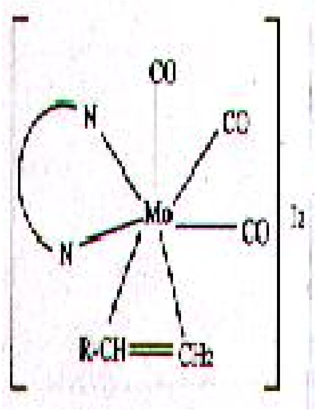
Many carbonyl compounds of group VIB elements of the periodic table were studied [24,25]. Gray and Beach [26,27] measured the UV absorption spectra of $M(CO)_6$ of group VIB elements and assigned the band on the MOT basis.

The new complexes are conducting and most diagnostic bands, their assignments are shown in table (4), fig (3).

The used solvent is chloroform ,causes blue shift for all absorption bands, the characteristic in the spectra of the complexes is the appearance of a new band at around (27.470)cm^{-1} which is not found in the spectrum of the parent (M) , this is assigned as IL' ($\pi - \pi^*$) for donor moieties of legends (olefin, nitrogen and sulfur atoms).

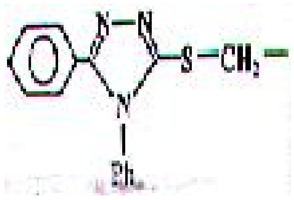
The absorption bands in high energy region can be assigned to the two components of ($\pi - \pi^*$) transitions of carbonyl groups .Besides that, the LF transition can't be assigned easily, since they may be overlap with that of ($\pi - \pi^*$) absorption bands [24,28,29].

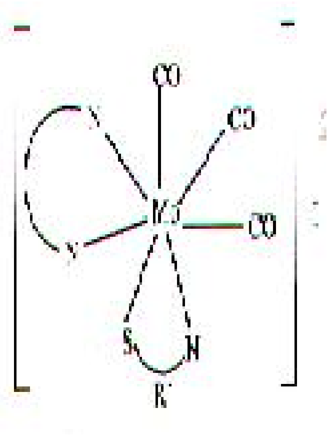
The general formula of the prepared complexes can be depicted as shown in table (1) and the proposed structures pentagonal bipyrmidal for the selected complexes can be given as follows:



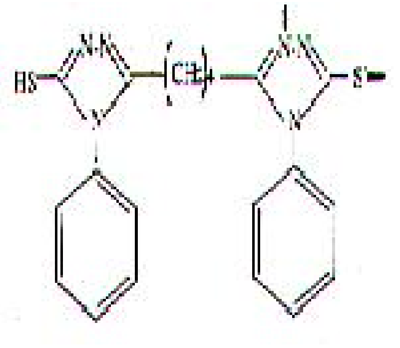
MI

Where R=

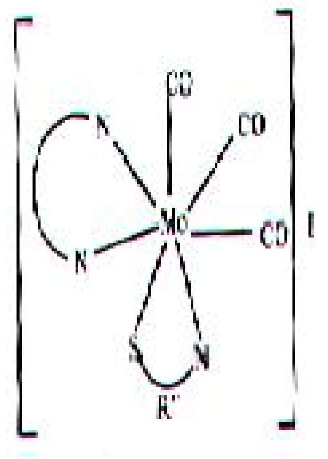




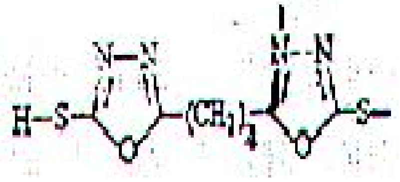
WhereR'=



MII



WhereR''=



MIII

References

1. Borg, S.J.; Bondin,M.I. ; Best,S.P. ; Razavet,M.; Liuand X. and Pickett,C.J. (2005), Biochemical Society Transactions Vol.33(1).
2. Okayran, S. O.; Kayran,C. and Kreiter,C. G. (1992),Organomet J. Chem., 434:79.
3. Rigaut,S.; Touchard, D. and Dixneuf, P.H. (2003), J.Organomet.Chem.,684:68.
4. Ammar,H.B.; Lenotre,G.; Salan, M.; Kaddachi, M.T .; Toupet,L.; Renaud,J.L.; Bruneau ,C. and Dixneuf, P.H. (2003), Eur.J.Inorg.Chem.,4055.
5. Jassim, A.H. (1993), Ph. D. Thesis,Al-Nahrain University of Engineering and Science Iraq.
6. Rasol N.(1987),M. Sc. Thesis, University of Baghdad ,Iraq and References Cited Therein.
7. AL-Zahawi,S. K. A.(1986), M. Sc. Thesis, University of the Baghdad Iraq .
8. Vahren Kemp,H. (1975), Angew. Chem. Int. Ed. Engl.,14:322 .
9. GreenWood ,N.N. and Earnshaw, A. (1998) "Chemistry of the Elements"Second Eddition , Pergamon Press.
10. Nesmeyanov ,A. N. and Nesmeganov, N.A . (1981),"Fundamental of Organic Chemistry" Vol. III, Mir Publishers, Moscow.
11. Mishar ,L. and Anjali, Jha, (1996) Indian J. of Chemistry,35A: 1001.
12.Cottonn ,F. A. and Willkinson ,G.S. (1987),"Advanced Inorganic Chemistry" Acomprehensive Text, Fifth Eddition, John. Wiley.
13. Abbas,M. H. (1991) Ph. D. Thesis, Nottingham.
14. Musa, F.H. (1998),Iraqi :J.of Chem.,Vol.24 (2).

15. Musa,F.H. ; Mahmoud ,M.J. and Mustafa,I.F. (2002),Ibn Al-Haitham , J.for Pure and Appl . Sci ., Vol . 15(3):44.
16. Stiddard,M. H. B. (1962) J. Chem. .Soc., 4712.
17. Nakamoto, K. (1997)," Infrared Spactro of Inorganic and Coordination Compounds", 6th. Ed. Wily, Intersience, New York.
18. Al-Obaidi, E. Z. M.; Nadir,K. M. and Eur. Roche, V. E .(1991)J. Med. Chem., 26.
19. Singh, B. and Singh, R. D. (1977), J. Inorg. Chem ., 39: 25.
20. Mustafa,I.F. ; Atto , A.T. and Musa, F.H. (1991),Iraq J.Chem., 16.
21. Dilsky Stefan and Schenk Wolfdieter,A. (2006) , Z.Naturforsch , 61b:570 .
22. ACotton,F. (1971)."Chemical Application of Group Theory"2nd.Ed.New York,Wiley Interscience.
23. Tripath ,S. C. and Srivastava ,S. C. (1970) J. Organomet. Chem., 25:193 .
24. Stoeffler,H.D.; Thornton,N.B.; Temkin, S.L; Schanze, K. S. (1995),J.Am.Chem. Soc., 117:7119
25. George, M.W. and Turner, J.J. (1998),Coord.Chem.Rev.,177:201.
26. Gray, H. B. and Beach,N.A. (1963) J. Am. Chem. Soc., 85:2922.
27. Beachand,N.A. and Grya,H.B. (1968),J.Amer.Chem .Soc.,90:5713.
28. Friedman,A.E.; Chamborn,J.C.; Sauvage,J.P.; Turro N.J. and Barton,J.K. (1990),J.Am.chem.soc.,112:4960.
29. Geoffroy,G.L. and Wrighton, M.S. (1979) "Organometallic Photochemistry " Academic Press. New York.

Table (1) Some Physical Properties of [Mo(CO)$_4$bipy] . (M) and new Prepared Complexes

	Colour	M.P.(C^0)	%Yield	Chemical Formula
M	**Red**	**(189-191)**	**95**	$C_{14}H_8N_2O_4Mo$
MI	**Deep brown**	**(244-246)**	**77**	$C_{30}H_{21}N_5O_3SMoI_2$
MII	**Orange**	**(280-282)dec.**	**75**	$C_{33}H_{28}N_8O_3S_2MoI$
MIII	**Brown**	**(174-176)**	**87**	$C_{21}H_{18}N_6O_5S_2MoI$

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Table (3) CO Vibrational Modes and their assignments for Cis-Mo $(CO)_4$-bipy and fac. Mixed ligand Molybdenum tri-carbonyl compounds

Compound	$A_1^{(2)}$	$A_1^{(1)}$	B_1	B_2
M	2012	1918	1887	1820
Compound	A_1	A'	A"	
MI	1967	1910	1869	
Compound	A_1	E		
MII	1991	1870		
MIII	1992	1890		

Where L= bipyridyl (bipy)

L'= triazole or oxadiazole group

Table (4): Electronic Spectra and Conductance (in $CHCl_3$) for Metal Carbonyl Complexes

Band nm (cm^{-1})(M)	Assignment	Band nm (cm^{-1})			Assignment	μscm^{-1}
		MI	MII	MIII		
486(20.576)	Mo→L CT	366(27.322)	365(27.397)	361(27.700)	π−π*IL'	80
370(27.027)	π−π*IL	331(30.211)	343(29.154)	343(29.154)	Mo→ π* COCT	50
343(29.154)	Mo→ π* COCT	255(39.215)	259(38.610)	254(39.370)	Mo→ π* COCT	50
256(39.062)	Mo→ π* COCT					

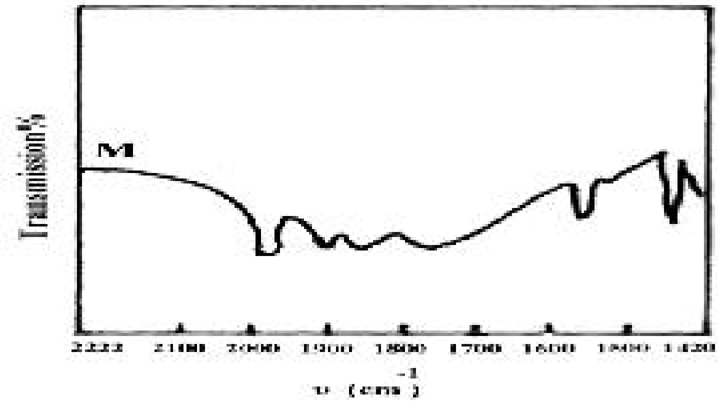

Fig. (1): The selected CO bands of tetracabonyls (Mo) in the stretching region

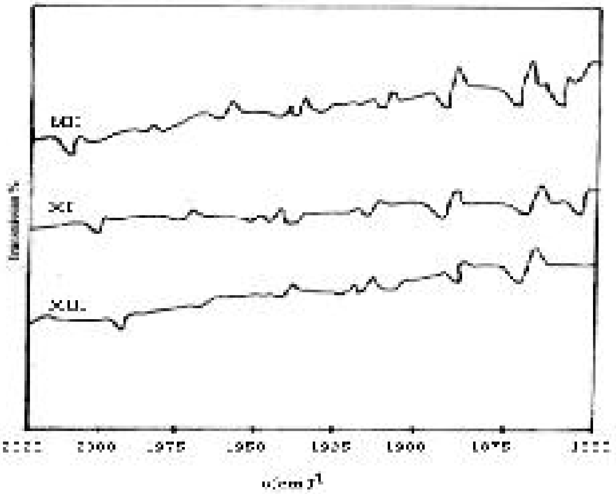

Fig. (2): Selected CO band of Mo complexes in the CO stretching region

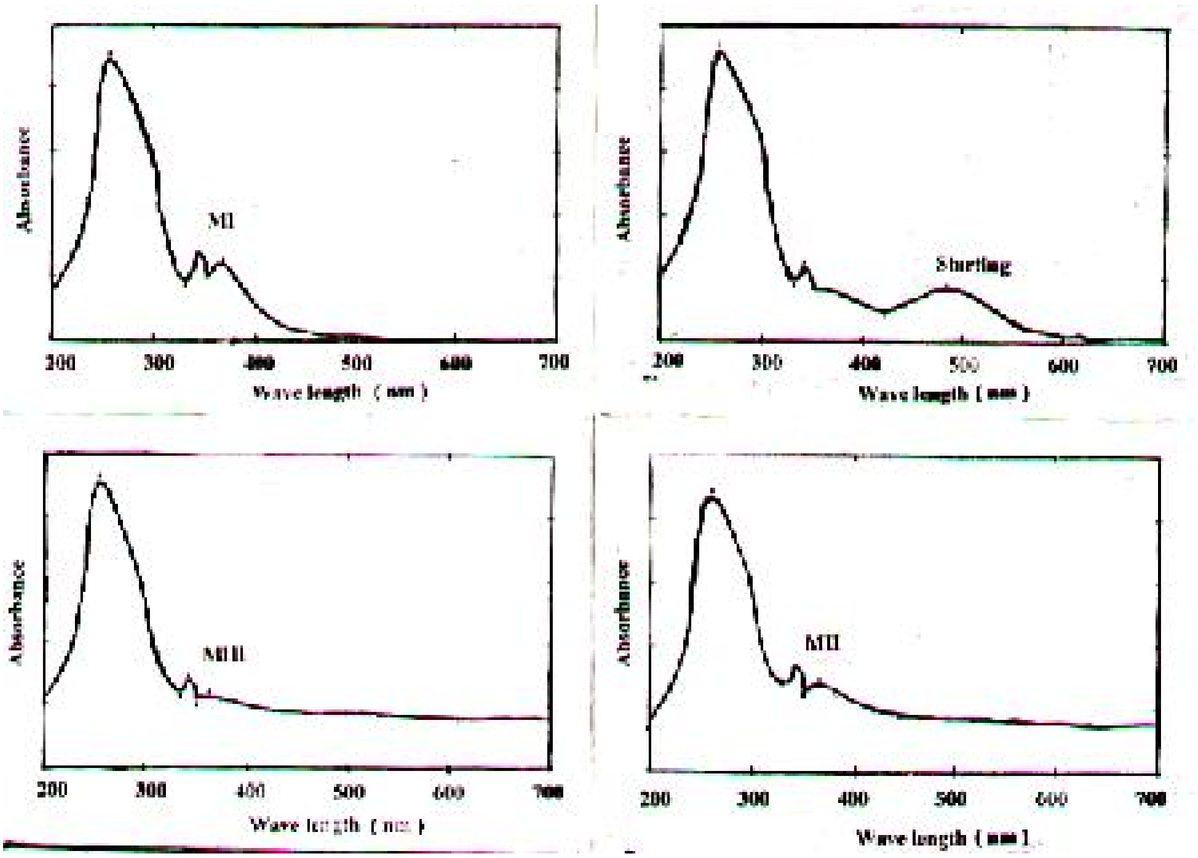

Fig. (3):Absorption spectra of $Mo(CO)_4$ bipy and their complexes in chloroform solvent

تحضير ودراسة تركيبية لبعض معقدات كاربونيلات الموليبدينيوم (II) مع مشتقات الترايازول والاوكسادايازول

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الخلاصة

حضرت عدد من المعقدات الكاربونيلية الجديدة الحاوية على مشتقات الترايازول والاكسادايازول تم تشخصيها واقتراح شكلها الهندسي بالطرائق الفيزيائية المناسبة بطيف الاشعة تحت الحمراء والاشعة فوق البنفجسية المرئية، التوصيلية الكهربائية فضلاً عن الطرائق الكيمائية القياسية والخواص الفيزيائية.

اعطت نتائج الدراسة بطيف الاشعة تحت الحمراء والاشعة فوق البنفسجية–المرئية مع الحسابات النظرية باستخدام نظرية المجموعة براهين اضافية مهمة للصيغ التركيبية المفترضة ونوع الارتباط في هذه المركبات.