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Synthesis and characterization of new chromium, molybdenum and tungsten complexes of 2-[2-(methylaminoethyl)] pyridine

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ABSTRACT

A green chemistry route of synthesis using direct sunlight irradiation for the reactions of [M(CO)$_6$] M = Cr, Mo or W with 2-[2-(methylaminoethyl)] pyridine (maepy) in THF. The reactions resulted in the formation of the oxo complex [Cr$_2$(O)$_4$(maepy)$_2$] (**1**) and the tetracarbonyl complexes [Mo(CO)$_4$(maepy)] (**2**) and [W(CO)$_4$(maepy)] (**3**). The prepared complexes were characterized by elemental analysis, IR, NMR, mass spectrometry and magnetic measurement. The complexes (**1**–**3**) were further investigated by thermogravimetric technique (TG). The biological activity of maepy and complexes as antibacterial and antifungal reagents have been investigated.

1. Introduction

Green chemistry, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances and the energy requirements. One of the principles that cover this concept is the design of energy efficient processes. Hence, energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure [1].

On the other hand, organometallic complexes of transition metal carbonyls with N-containing heterocycles have been the subject of considerable interest in recent years. Their photochemical and electronic properties and potential for industrial applications have led to many studies for the use as photo-sensitizers, catalysts and conducting coordinating polymers [2–4]. Many metal carbonyl derivatives are used in photochemical, photochromic, and thermochromic processes [5]. On the other hand, pyridine derivatives have biological and pharmaceutical importance [6,7]. Oxidation–reduction of pyridine derivatives plays important roles in biological activity [8]. These derivatives are characterized by their antiviral, antifungal, antioxidant, antithyroid, and diuretic action. Some pyridine complexes act as active catalysts for olefin polymerization [9]. Tungsten is known as a biologically active metal for several years. Although tungsten is not considered as one of the essential elements required by most organisms, it is a biologically active metal and required as component for some enzyme activity. Molybdenum or tungsten is present at the active sites of over 30 distinct enzymes [10,11].

To continue our investigation of the reactions of group 6 metals with various ligands, here we report the reactions of [M(CO)$_6$] M = Cr, Mo or W with 2-[2-(methylaminoethyl)] pyridine (maepy) (Scheme 1), using sunlight irradiation; a sustainable source of energy, as a route of green chemistry synthesis compared with the traditional reflux route.

2. Experimental

2.1. Materials and reagents

Cr(CO)$_6$, Mo(CO)$_6$ and W(CO)$_6$ were purchased from Fluka. 2-[2-(methylaminoethyl)] pyridine was supplied by Aldrich. All solvents were of analytical grade.

2.2. Measurements

Infrared measurements using KBr pellets were carried out on a Unicam-Mattson 1000 FT-IR spectrometer. Magnetic measurements of the complexes in the solid state (Gouy method) were carried out using a Sherwood magnetic susceptibility balance. ^{1}H NMR measurements were performed on a Varian-Mercury 300 MHz spectrometer. Elemental analyses for carbon, hydrogen,

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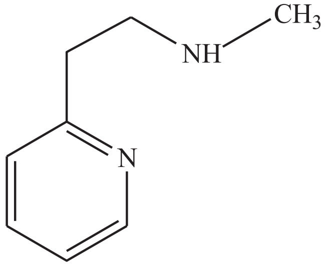


Scheme 1. 2-[2-(Methylaminoethyl)] pyridine (maepy).

and nitrogen (CHN) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectrometry measurements of the solid complex were carried out on a JEOL JMS-AX 500 spectrometer. Thermogravimetric (TG) analyses were carried out under nitrogen atmosphere with a heating rate of 10 °C min^{-1} using a Shimadzu DT-50 thermal analyzer.

2.3. *Sun irradiation synthesis of [$Cr_2(O)_4(maepy)_2$] complex (**1**)*

A mixture of $Cr(CO)_6$ (0.2 g, 0.90 mmol) and maepy (0.12 g, 0.89 mmol) in 30 ml THF, in sealed 50-ml tubes, was exposed to unaided sunlight irradiation for 10 h; The tubes were hanged horizontally from both sides in a way to not obstruct sunlight to go through the tubes. The reaction resulted in the formation of a brown precipitate. Comparatively, a mixture of [$Cr(CO)_6$] (0.2 g, 0.90 mmol) and maepy (0.12 g, 0.89 mmol) in 30 ml THF was refluxed for 11 h where a brown precipitate was also separated. The isolated green precipitates from both routes of synthesis were washed several times by hot THF, left to dry and kept at vacuum desiccators.

2.4. *Synthesis of [$Mo(CO)_4(maepy)$] complex (**2**) and [$W(CO)_4(maepy)$] complex (**3**)*

Similar procedure to that used for the preparation of [$Cr_2(O)_4(maepy)_2$] (**1**) was employed for the preparation of [$Cr_2(O)_3(maepy)_2$] (**2**) and [$W(CO)_4(maepy)$] (**3**) complexes (the reaction time and yield were reported in Table 1).

2.5. *Biological activity*

Antibacterial activity of 2-[2-(methylaminoethyl)] pyridine (maepy) and its complexes [$Cr_2(O)_4(maepy)_2$] (**1**) [$Mo(CO)_4(maepy)$] (**2**) and [$W(CO)_4(maepy)$] (**3**) were determined using a modified Kirby–Bauer disk diffusion method [12]. Plates incubated with filamentous fungi as *Aspergillus flavus* at 25 °C for 48 h. Gram-positive bacteria as *Staphylococcus aureus* and gram-negative bacteria as *Escherichia coli* were incubated at 30 °C for 24–48 h. The diameters of the inhibition zones were measured in millimeters. The samples were repeated three times from which the inhibition was averaged.

3. Results and discussion

Interaction of [$M(CO)_6$] M = Cr, Mo and W with 2-[2-(methylaminoethyl)] pyridine (maepy) in THF gave [$Cr_2(O)_4(maepy)_2$] (**1**), [$Mo(CO)_4(maepy)$] (**2**) and [$W(CO)_4(maepy)$] (**3**) complexes. Table 1 summarizes the reaction conditions for the two routes of synthesis. The sunlight irradiation route resulted in lower yield compared with the reflux method but the former has the advantages of using a cheaper and sustainable source of energy. Although the sunlight irradiation is used in this work only as a synthesis route, this may give some attention for further research on the role of light in the reaction, the nature of interaction (photochemical or photothermal) and which part of the light efficiently induces such reactions.

3.1. *Elemental analysis*

Elemental analyses of the complexes resulted from the two routes of syntheses were found to be very similar and in good agreement with that calculated for the proposed formulae. The results of the elemental analysis of the complexes resulted from the sunlight irradiation are given in Table 1.

3.2. *Mass spectra of complexes*

The mass spectral data of the complexes showed the major mass fragmentation peaks. The parent ion peak at $m/z = 424$ for chromium complex (**1**) which is coincident with the parent-O species. On the other hand, for molybdenum complex (**2**) the parent ion peak at $m/z = 340$ correspond to $[P–4H]^+$ and the tungsten complex (**2**) showed the parent ion peak at $m/z = 432$ due to the molecular weight (Table 1). It is interesting to highlight the contribution of the different isotopes of chromium, molybdenum and tungsten to the molecular mass of their complexes. This is clear in the mass fragmentation peaks due to the elements. For chromium, a close two fragmentation peaks were observed at $m/z = 51$ (74.28%) and 52 (17.58%), this is in addition to the Cr_2 species observed at $m/z = 104$ (7.88%) and 106 (15.17%). Tungsten showed also close mass fragmentation peaks with $m/z = 182$ (6.96%), 183 (5.37%), 184 (11.15%) and 186 (14.02%) corresponding to the known stable W isotopes. It is worthy to mention that the resolution of mass fragmentation patterns of [$Mo(CO)_4(maepy)$] (**2**) did not enable us to trace the Mo isotopes.

3.3. *IR spectra*

The IR spectra of the complexes were compared with the free ligand (maepy) in order to determine the coordination sites that may be involved in chelation. The characteristic peaks of maepy ligand and its complexes are listed in Table 2.

The IR spectrum of the 2-[2-(methylaminoethyl)] pyridine ligand (maepy) showed a broad band at 3305 cm^{-1} which assigned to the stretching vibration of NH group. This band has been found to be shifted to higher wave numbers in the spectra of

Table 1
Analytical data of the complexes (**1**–**3**).

	% yield		Reaction time (h)		M.wt.	Mass spectra m/z	% C Calc. (found)	% H Calc. (found)	% N Calc. (found)
	Reflux	Sunlight[a]	Reflux	Sunlight[a]					
[$Cr_2(O)_4(dap)_2$]	75.00	65.00	11.00	10.00	440.38	424 (P-O)	43.64 (43.75)	5.49 (4.90)	12.72 (12.50)
[$Mo(CO)_4(maepy)$] (**2**)	77.50	46.00	7.00	7.00	344.20	340 (P–4H)	41.87 (42.00)	3.51 (3.98)	8.14 (8.21)
[$W(CO)_4(maepy)$] (**3**)	76.00	63.50	5.50	5.00	432.09	432 (P^+)	33.33 (33.91)	3.51 (3.00)	6.48 (6.31)

[a] The reactions had been carried out in Cairo, April 2008; average temperature = 31 °C and the weather at the time of reactions was sunny.

Table 2
Important IR data of molybdenum and tungsten of complexes with (maepy).

Compound	IR (cm^{-1})						
	υ(NH)	υ(CO)	υ(C=N)	υ(M=O)	υ(M—O)	δ(py)	υ(M—N)
maepy	3305(b)	–	1569(s)	–	–	605(w)	–
[$Cr_2(O)_4(maepy)_2$] (**1**)	3401(b)	–	1605(m)	995(w), 914(w)	837(w)	693(w)	515(w)
[$Mo(CO)_4(maepy)$] (**2**)	3427(s)	2007(m), 1888(m) 1855(m), 1799(m)	1594(w)	–	–	731(m)	470(w)
[$W(CO)_4(maepy)$] (**3**)	3414(b)	2004(m), 1877(w) 1811(s), 1730(m)	1594(s)	–	–	683(m)	612(m)

b, broad; m, medium; s, strong; w, weak.

complexes (3401–3427 cm^{-1}). The shift in band position is an indication of the participation of NH in coordination to the metal ions under investigation without proton displacement [13]. Furthermore, the spectrum of (maepy) exhibited a band due to υ(C=N) pyridyl ring [14,15] which was found to be shifted to higher wave number in the spectra of complexes [16–19]. Also, the IR spectra of [$Cr_2(O)_4(maepy)_2$] (**1**), [$Mo(CO)_4(maepy)$] (**2**) and [$W(CO)_4(maepy)$] (**3**) complexes displayed shifted bands due to the in-plane ring deformation (δ(py)) in the range of 683–731 cm^{-1} indicating the participation of the pyridyl ring in coordination. Thus, the maepy behaves as bidentate ligand in complex formation. In addition, [$Cr_2(O)_4(maepy)_2$] (**1**) complex showed band at 995 cm^{-1} due to Cr=O stretching vibration [20]. The infrared spectrum of the chromium complex exhibited also band at 837 cm^{-1} which characteristic to Cr—O—Cr stretching vibration [20]. Also, the complex displayed band at 515 cm^{-1} which is assigned to Cr—N bond [19]. The infrared spectra of the molybdenum and tungsten complexes exhibited four bands in the range of 1730–2007 cm^{-1}, due to the presence of four CO in the terminal metal carbonyl region [13,21–23]. In addition, the IR spectrum of the molybdenum and tungsten complexes showed bands at 470 cm^{-1}, 612 cm^{-1} due to M—N bonds [19].

3.4. Magnetic measurements

The magnetic susceptibility measurements of the [$Cr_2(O)_4(maepy)_2$] (**1**) complex in the solid state at 298 K showed a value of 2.79×10^{-5} e.m.u. g^{-1} with an effective magnetic moment of 5.43 BM. However, the corresponding value for each chromium (2.72 BM) is less than the spin-only moment of two unpaired electrons (2.83 BM). The observed μ_{eff} may indicate the existence of the complex as a binuclear species with strong antiferromagnetic coupling between the two metal centers. The dimeric structures of the chromium complex was further confirmed from the thermogravimetric analysis and mass spectra (m/z = 424; P$^+$–O) (*vide supra*).

The magnetic susceptibility measurements for [$Mo(CO)_4(maepy)$] (**2**) and [$W(CO)_4(maepy)$] (**3**) indicated their diamagnetic nature. This is confirmed also from the ^{1}H NMR spectra of complexes (*vide infra*). In the low spin octahedral molybdenum and tungsten complexes with $t_2g^6eg^0$ configuration is expected to be diamagnetic [13].

3.5. ^{1}H NMR spectra

The ^{1}H NMR of (maepy) in deuterated DMSO ligand showed a singlet at 8.47 ppm, which has been assigned to NH proton and multiplets at 7.66–7.12 ppm, which has been assigned to the aromatic protons of the pyridine ring. In addition, the ligand showed two doublets at 3.00 ppm and 2.85 ppm with an integration of 4 protons, which has been assigned to the protons of the two CH_2 groups. It also displayed a singlet at 2.27 ppm which is assigned to the protons of CH_3 group.

The ^{1}H NMR spectrum of the isolated [$Mo(CO)_4(maepy)$] (**2**) and [$W(CO)_4(maepy)$] (**3**) complexes showed similar signals to maepy ligand with appropriate shift as a result of complexation. The ^{1}H NMR of the [$Mo(CO)_4(maepy)$] (**2**) showed singlet at 7.42 ppm due to NH proton and multiplets in the range of 5.71–4.44 ppm for aromatic protons of the pyridine ring. Similarly, the ^{1}H NMR of the [$W(CO)_4(maepy)$] (**3**) exhibited singlet at 8.50 ppm for NH proton and showed multiplets at 5.87–4.44 ppm for aromatic protons of the pyridine ring (Table 3). These findings indicate that both NH and pyridine nitrogen participated in the coordination to metals. The shifts of the other signals may be due to the change in the electronic system of the ligand upon complex formation [13].

Table 3
Important ^{1}H NMR data for the maepy ligand and their complexes.

Compound	^{1}H NMR (ppm)
maepy	8.47s (1H, NH), 7.66–7.12m (4H, pyridine), 3.00–2.74m (4H, CH_2), 2.27s (3H, CH_3).
[$Mo(CO)_4(maepy)$] (**1**)	7.42s (1H, NH), 5.94–5.71m (4H, pyridine), 3.44–3.42m (4H, CH_2), 2.56s (3H, CH_3).
[$W(CO)_4(maepy)$] (**3**)	8.50s (1H, NH), 5.87–4.44m (4H, pyridine), 3.30–2.97m (4H, CH_2), 2.49s (3H, CH_3).

m, multiple; s, singlet.

3.6. Thermal analyses

The reported chromium, molybdenum and ruthenium complexes (**1–3**) were found to be air stable and have higher thermal stability. These properties along with their possibility to use as catalysts in epoxidation reactions have prompted us to investigate their thermal decomposition [24]. In addition, a deeper insight on the structures of the investigated complexes was undertaken using thermogravimetry (t.g.) and derivative thermogravimetry (d.t.g.) techniques (Figs. 1 and 2). The detailed thermal decomposition data for chromium (**1**) and tungsten (**3**) were given in Table 4.

[$Cr_2(O)_4(maepy)_2$] (**1**) complex (m/e = 424; 5%) decomposed in three thermal steps (Fig. 1) covering the temperature 474–845 K. The first decomposition step occurred at 474–520 K with a weight loss of 7.22% (7.27% calc.). The percentage loss was consistent with the elimination of one O_2 molecule assigned as the removal of the di-oxo bridges. The second decomposition peak occurred at 641–674 K with a weight loss of 34.30% (34.50% calc.) could

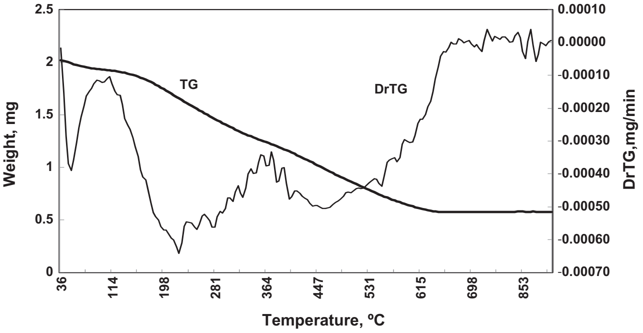


Fig. 1. TG and DrTG plot of [$Cr_2(O)_4(maepy)_2$] complex.

Table 4
Thermal data for the complexes of chromium and tungsten with (maepy) ligand.

Molecular formula	M.wt.	DTG_{max} (K)	Decomposition temperature (K)	Weight loss %	Mass loss		Eliminated species	Metallic residue %
					Calc.	Found		
$[Cr_2(O)_4(C_8H_{12}N_2)_2]$	440.38	495	474–520	7.22	32.00	31.80	O_2	2Cr (23.6%)
		657	641–674	34.30	151.80	151.00	$C_9H_{15}N_2$	
		824	795–845	35.00	154.60	154.00	2O, $C_7H_9N_2$	
$[W(CO)_4(C_8H_{12}N_2)]$	432.09	412	392–492	12.80	55.40	56.00	2CO	W (42.8%)
		464	523–773	44.30	191.0	192.00	2CO, $C_8H_{12}N_2$	

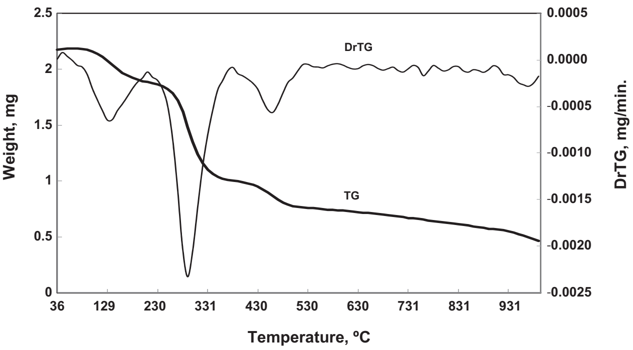


Fig. 2. TG and DrTG plot of $[W(CO)_4(maepy)]$complex.

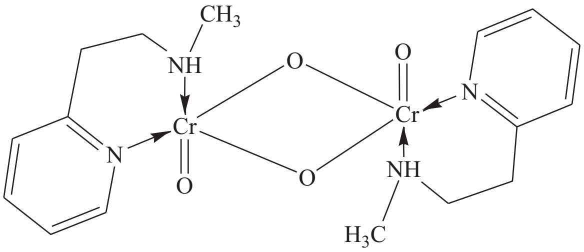
be attributed to the loss of $C_9H_{15}N_2$ species (mass loss = 151; $m/e = 150$; 13.69%). The third decomposition peak observed in the temperature range of 795–845 K with a weight loss of 35.00% (35.10% calc.) which may be assigned for the removal of the rest of the ligand molecule (mass loss = 154; $m/e = 154$; 8.74%) leaving 2Cr (23.6%) as the metallic residue (mass loss = 103.93; $m/e = 52$; 17.58% and $m/e = 102$; 21.56%).

The thermogram of $[W(CO)_4(maepy)]$ displayed three successive decomposition steps (Fig. 2). The first decomposition peak occurred at 372–492 K with weight loss of 12.8% (12.9% calc.) (mass loss = 56; $m/e = 55$; 17.9%) was assumed to the loss of two CO groups. The second and third peaks were existed over a wide temperature range of 523–773 K, with a net mass loss of 44.3% (44.4% calc.) (mass loss = 192; $m/e = 192$; 5.85%) which may be due to the elimination of other two CO groups along with $C_8H_{12}N_2$ species to yield finally the metallic tungsten as residue (42.8%) (mass loss = 184.93; $m/e = 184$; 11.15%).

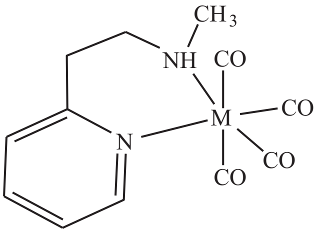
3.7. Structural interpretation

On the basis of the above observations, the structures of the complexes are shown in Schemes 2 and 3.

It is interesting to explain that the oxocomplexes of chromium complex were passed through the intermediate $Cr(CO)_3(maepy)$ (I) which upon reaction with oxygen would result in the formation of the final product (III) Cr(IV) (Scheme 4). This mechanism is proposed for many of group 6 complexes [13,25,26].



Scheme 2. The proposed structure of $[Cr_2(O)_4(maepy)_2]$.



Scheme 3. The proposed structure for $[M(CO)_4(maepy)]$ where M = Mo or W.

3.8. Antimicrobial activity

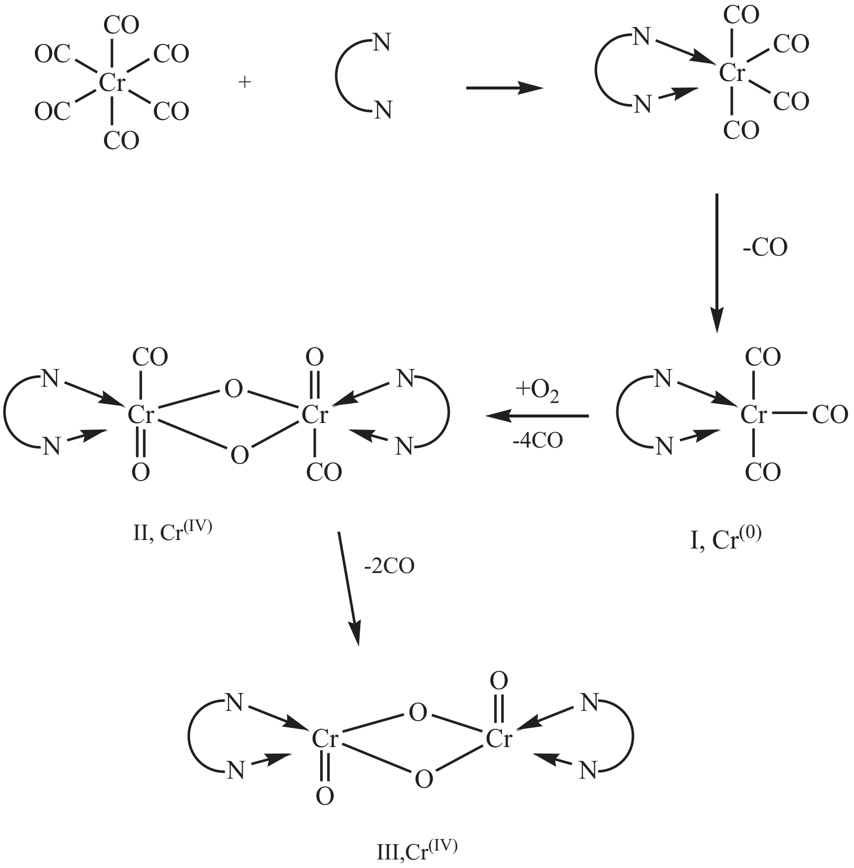
Antimicrobial activities of (maepy) and its $[Cr_2(O)_4(maepy)_2]$ (**1**), $[Mo(CO)_4(maepy)]$ (**2**) and $[W(CO)_4(maepy)]$ (**3**) complexes have been carried out against *S. aureus* as gram-positive bacteria, *E. coli* as gram-negative bacteria and both *A. flavus* and *Candida albicans* as fungi, using a modified Kirby–Bauer disk diffusion method [12]. The tetracycline as antibacterial agent and amphotericin B as antifungal agent were used as standards. The mean inhibition values as well as the error limits are given in Table 5.

The (maepy) ligand has been found to be the most active against fungi (*C. albicans* and *A. flavus*) as compared with the metal complexes and standard. Moreover, $[Mo(CO)_4(maepy)]$ complex show considerable activity against *C. albicans* fungi in contrast with

Table 5
Antimicrobial activity of (maepy) ligand and its complexes.

Compound	Zone of inhibition (mm/mg sample) (error limit)[a]			
	Escherichia coli (Gram-negative)	*Staphylococcus aureus* (Gram-positive)	*Aspergillus flavus* (Fungus)	*Candida albicans* (Fungus)
maepy	21(2.3)	23(1.45)	23(2.1)	25(1.94)
$[Cr_2(O)_4(maepy)_2]$ (**1**)	11(1.12)	11(1.67)	0	0
$[Mo(CO)_4(maepy)]$ (**2**)	13(2.4)	16(3.1)	0	18(1.2)
$[W(CO)_4(maepy)]$ (**3**)	11(2.3)	12(1.2)	0	0
Tetracycline Antibacterial agent	32(2.1)	30(2.4)	–	–
Amphotericin BAntifungal agent	–	–	16(1.1)	17(1.7)

[a] Error limit = (maximum value – minimum value).



Scheme 4. Proposed mechanism for the formation of Cr oxocomplex.

chromium and tungsten complexes which have no activity against fungi. The maepy ligand has higher activity than its complexes (**1**–**3**) towards both gram-positive and gram-negative bacteria. The complexes have activities very close to each other and far from both ligand and standard which may be due to their limited solubility in most of the solvents.

4. Conclusion

The direct sunlight irradiation synthesis for the reactions of $[M(CO)_6]$ M = Cr, Mo or W with 2-[2-(methylaminoethyl)] pyridine (maepy) in THF may stand as a feasible and sustainable method of synthesis of metal carbonyl-organic systems.

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