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Photochemical Reaction of Metal Carbonyls $[M(CO)_6(M=Cr,Mo,W)]$ with 2-acetyl-5-chlorothiophenemethanesulfonylhydrazone

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Abstract
The new complexes, $[M(CO)_5(msh4)](Cr(1),Mo(2),W(3))$, have been synthesized by the photochemical reaction of metal carbonyls with 2-acetyl-5-chlorothiophenemethanesulfonylhydrazone(msh4) .The structure of these complexes has been investigated by using elemental analyses; FT-IR; EI-MS and ^{1}H NMR spectrometric methods. According to all spectroscopic data, msh4 is monodaentate and coordinate via thiophene ring sulfur.

Keywords
Metal carbonyls; Methanesulfonylhydrazone; Photochemical Reactions.

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1. INTRODUCTION

The importance of sulfonamide was reported to be the first antibacterial drug [1, 2]. Many sulfonylamide derivatives exhibit a cytostatic effect and find application in cancer chemotherapy [3, 6]. Methanesulfonamide residue has a appeared as a suitable pharmacophoric equivalent to replace functional groups in drug design. Many compounds containing a hydrazine fragment, e.g. carboxylic acid hydrazides and their Schiff bases, have shown cytostatic activity [7]. Methanesulfonic acid (msh), $CH_3SO_2NHNH_2$, is the simplest organic representative of the compounds containinig both sulfonamide and hydrazine. Structure and vibrational spectroscopy of msh were reported by Lenco et al. [8].

The literature is rich with transition metal-thiophene complexes containing thiophene ligands bound in many ways $(i.e.\eta^1,\eta^2,\eta^3,\eta^4,\eta^5,and\eta^6)$ to a variety of metal centers, but organometallic complexes of group VIB metals containing thiophene ligands are still relatively rare . Only two Mo complexes containing coordinated thiophene ligands have been reported. The first reported stable Mo–thiophene complex, $[Mo(CO)_3(2,5-(Ph_2PCH_2CH_2)_2C_4H_2S]$, exists as a pair of chelating ligands that are bound to Mo through the phosphine groups and sulfur. The second complex, $[Mo(\eta^6-2MeBT)_2]$, is a sandwich complex consisting of a Mo coordinated to two 2-methylbenzothiophene (2-MeBT) ligands through the arene rings in an η^6 fashion [9].

As ligands, methanesulfonylhydrazones, thiophene-2-carboxyaldehyde methane sulfonylhydrazone (msh 1), 2-acetyl thiophene methane sulfonyl hydrazone (msh 2), and 2-acetyl-5-methyl thiophene methane sulfonyl hydrazone (msh 3) and their metal carbonyl complexes have reported. In addition, structure and vibrational spectroscopy of msh, msh 1 ,msh 2, and msh 3 were reported [10].

In this work, first, the synthesis of 2-acetyl-5-chlorothiophenemethanesulfonylhydrazone (msh 4) were reported. Then, the new complexes $[M(CO)_5(msh4)](M=Cr(1),Mo(2),W(3))$ as shown Figure 1 were prepared by the photochemical reactions of $[M(CO)_6](M=Cr,Mo,W)$ with msh 4 and characterized elemental analysis, mass spectrometry, IR, and ^{1}H NMR spectrocopy. According to all the spectroscopic data, msh 4 is monodentate and coordinated via thiophene ring sulfur (C–S–C) in the complexes. Analytical data of the complexes are given in the experimental section.

2. EXPERIMENTAL SECTION

2.1 Materials and instrumentation

Elemental analysis was performed using LECO-CHNS-O-9320 model (TUBİTAK Laboratories, ANKARA). The infrared spectra of the compounds were recorded on samples in hexane at the Ege University with a Mattson 1000 FT-IR spectrometer. ^{1}H NMR spectra were recorded in DMSO-d6 on a 400 MHz High Performance Digital FT-NMR at TUBİTAK. Electron impact mass spectra were recorded on a Micromass VG Platform-II LC-MS at TUBİTAK. UV irradiations were performed with a medium-pressure 400 W mercury lamp through a quartz-walled, immersion-well reactor.

The solvents, pentane, benzene, hexane, dichloromethane, acetone, ethyl alcohol, diethylether, hydrazine hydrate, and silica gel were purchased from Merck and M(CO)6 (M=Cr,Mo,W) from Aldrich. These reagents were used as supplied. Methane sulfonyl chloride, hydrazine mono hydrate,and 2-acetyl-5-chlorothiophene were commercial products(purum).The solvents used were purified and distilled according to routine procedures [11].

2.2 Preparation of heteroaromatic methanesulfonylhydrazone

The preparation of heteroaromatic methanesulfonylhydrazone 4 is similar to that applied by Dodoff [12]. Thus, solution of 2.20 g (0.02 M) of msh is dissolved in 10 mL of ethanol. Then, the solution that 3.00 g (0.03 M) of the corresponding carbonyl compound (2-acetyl-5-chlorothiophene) dissolved in 10 mL of ethanol is added. The mixture is stirred for 30 min. The precipitating product is kept overnight in a deep freze and then filtered. The precipitate is recrystallized from water and filtered, followed by rinsing with ether. Finally, it is dried on P_2O_5 in a vacuum desicator.

2.2.1 Synthesis of 2-acetyl-5-chlorothiophenemethanesulfonylhydrazone (msh 4):

Yield(76%). Anal.Calcd. C, 33.28; N, 11.08; S, 25.38; H, 3.56. Found C, 35.42; N, 11.22; S, 25.46; H, 3.72. IR(υ, KBr): 3198(s,NH), 3036(w,CH_{ring}), 1600(m,CN), 1331(s,$(SO_2)_{asym}$), 1170(s,$(SO_2)_{sym}$), 896(m,CSC_{ring}), 704(m,CS_{sym}), 590(m,CS_{asym}). ^{1}H NMR (δ, DMSO)= 2.20 ($CH_3C=N,3H$, s); 3.01(CH_3SO_2, 3H, s); 7.10(CH_{ring}, 1H, s); 7.24(CH_{ring},1H, s); 9.98(NH, 1H, s).

2.3 Synthesis of metal carbonyl complexes

The complexes, $[M(CO)_5(msh4)](M=Cr(1),Mo(2),W(3))$ were prepared by photochemical reactions metal carbonyls $M(CO)_6(M=Cr,Mo,W)$ with msh 4 and were obtained in 70-80% yields. The methods employed fort he preparations of the complexes are very similar , so that the preparation of $[Cr(CO)_5(msh4)](1)$ is given in detail as a representative example.

2.3.1 $Cr(CO)_5(msh4)(1)$:

$Cr(CO)_6$ (0.44g, 2 mM) and msh4 (0.25g, 1 mM) were dissolved in tetrahydrofuran (80-100 mL). The solution was irradiated for 2 h using a 400 W medium-pressure mercury lamp through a quartz-walled immersion well reactor. During the irradiation, the color of the reaction mixture changed from colorless to light Brown. After irradiation, the reaaction mixture was evaporated under vacuum, yielding a light brown solid. After dissolving in dichloromethane (10 mL), 50 mL of petroleum ether was added, resulting in precipitation of a light brown solid which was washed with petroleum ether and dried under vacuum.Traces of unreacted hexacarbonylchromium were sublimed out in vacuum on a cold finger at -20°C. The composition of compounds is confirmed by elemental analysis. Yield: (76%). Found (%): C, 32.96; H, 2.40; N, 6.72; S, 14.88. Calcd. for $CrC_{12}H_9N_2O_7S_2Cl$ (%): C, 32.41; H, 2.02; N, 6.30; S, 14.4. IR (υ, KBr): 2070(w, CO), 1938(br, CO), 1880(sh, CO), 950(s, CSC_{ring}), 868(m, CSC_{ring}), 620(m, CS_{sym}), 570(s, CS_{asym}) cm^{-1}. ^{1}H NMR(δ, DMSO-d_6): 2.18 ($CH_3C=N,3H$, s); 3.01($CH_3SO_2,3H$, s); 7.14 (CH_{ring}, 1H, s); 7.35 (CH_{ring},1H, s); 9.96 (NH,1H,s) ppm. MS(LC,70 eV): m/z(%)= 402(18)[M$^+$-(Me$^+$CO)]; 374(20)[M$^+$-(Me-2CO)]; 346(16)[M(Me-3CO)]; 318(10)[M$^+$-(Me-4CO); 290(12)[M$^+$-(Me-5CO).

2.3.2 $Mo(CO)_5(msh4)(2)$:

A similar synthetic procedure as that used for 1 was used expect that $Cr(CO)_6$ was replaced by $Mo(CO)_6$, giving pale-yellow crystals. Yield(58%). Found(%): C, 30.12; H, 2.02; N, 6.04; S, 13.66. $MoC_{12}H_9N_2O_7S_2Cl$ (%): C, 29.50; H, 1.84; N, 5.73; S, 13.12. IR (υ, KBr): 2073(w, CO), 1940(br, CO), 1888(sh, CO), 957(s, CSC_{ring}), 866(m, CSC_{ring}), 620(m, CS_{sym}), 578(s, $CSasym$) cm^{-1}. ^{1}H NMR(δ, DMSO-d_6): 2.18($CH_3C=N,3H$, s); 3.01($CH_3SO_2,3H$, s); 7.16 ($CH_{ring},1H$, s); 7.34 ($CH_{ring},1H$, s); 9.98 (NH,1H,s) ppm. MS(LC,70 eV): m/z(%)= 446(20)[M$^+$-(Me$^+$CO)]; 418(18)[M$^+$-(Me-2CO)]; 390(21)[M$^+$-(Me-3CO)]; 362(14)[M$^+$-(Me-4CO); 334(10)[M$^+$-(Me-5CO).

2.3.3 $W(CO)_5(msh4)(3)$:

A similar synthetic procedure as that used for 1 was used expect that $Cr(CO)_6$ was replaced by $W(CO)_6$, giving pale-yellow crystals. Yield(56%). Found(%): C, 25.88; H, 1.82; N, 4.96; S, 11.64. $WC_{12}H_9N_2O_7S_2Cl$ (%): C, 25.00; H, 1.56; N, 4.85; S, 11.12. IR (υ, KBr): 2072(w, CO), 1930(br, CO), 1880(sh, CO), 958(s, CSC_{ring}), 868(m, CSC_{ring}), 612(m, CS_{sym}), 580(s, $CSasym$) cm^{-1}. ^{1}H NMR(δ, DMSO-d_6): 2.18($CH_3C=N,3H$, s); 3.01($CH_3SO_2,3H$, s); 7.11 ($CH_{ring},1H$, s); 7.30 ($CH_{ring},1H$, s); 9.98 (NH,1H,s) ppm. MS(LC,70 eV): m/z(%)= 533(15)[M$^+$-(Me$^+$CO)]; 505(22)[M$^+$-(Me-2CO)]; 477(20)[M$^+$-(Me-3CO)]; 449(10)[M$^+$-(Me-4CO); 421(10)[M$^+$-(Me-5CO).

3. RESULTS AND DISCUSSION

3.1 Synthesis

The analytical results and some physical properties of the new heteroaromatic methanesulfonylhydrazone **msh 4** is summarized. It is colorless crystalline solid, stable at room temperature, and soluable in methanol, ethanol, THF, CH_2C_l2, DMSO, and poorly soluable in benzene and water.

3.2 Spectroscopic characterization

The assignment of the FTIR bands were made taking into consideration literature data for compounds containing appropriate structural fragments: sulfonamides [13, 17], sulfonyl hydrazines, and sulfonylhydrazones [12, 18, 20], methanesulfonyl derivatives [21, 24], and Schiff bases of salicylaldehyde, and related compounds [25, 29]. Infrared revealed that absorption due to C=O of the free ligand is 1610-1590 cm^{-1} [12]. The N-H absorption appeared at 3230-3180 cm^{-1}. The observed band at 520-320 cm^{-1} correspond to C-Cl stretching vibrations [30]. The medium C-S-C asymmetric stretch is 850-800 cm^{-1} [31].

^{1}H NMR data of DMSO-d_6 solutions of the msh 4 (2-acetyl-5-chlorothiophenemethanesulfonylhydrazone) is collected in the experimental section. The comparison of spectra of ketone derivatives facilities distinguishing the signals of the methyl protons from $CH_3-C, CH_3C=N, and CH_3SO_2$ fragments, the assignment of the latter being in accord with the data reported [12]. The signal of the $CH_3C=N$ protons show no splitting, and the positions of signals of the ring protons are typical.

The carbonyl complexes, $[M(CO)_5(msh4)](M=Cr,Mo,W)(msh4=2-acetyl-5-chlorothiophenemethanesulfonylhydrazone)$ were prepared by a photochemical reaction as shown in Figure 1. The photogeneration of $M(CO)_5$ from $M(CO)_6(M=Cr,Mo,W)$ has been extensively studied. These 16-electron $M(CO)_5$ fragments react quickly with any available donor to form $M(CO)_5$L species. The spectroscopic studies show that msh 4 monodentate coordinating via the thiphene ring sulfur(C-S-C) in the complexes. Analytical data of the complexes are given in the experimental section.

Important infrared spectral data of the complexes are presented in the synthesis section.Spectral shifts observed for a number of peaks in the vibrational spectra of msh 4 ligand are significant. The medium intensity band at 890 cm^{-1} observed in free ligand ascribed to $\upsilon(CSC)_{ring}$ stretch is divided in two bands, to higher values with 50 cm^{-1} and to lower values with 50 cm^{-1} for all compounds, suggesting involvement of sulfur in the bonding with metal [32]. The bands assigned to symmetric $\upsilon(C-S)$ and asymmetric $\upsilon(C-S)$ shift to lower frequency after complexation in all complexes. No shifts were observed at $\upsilon_{asym}(SO_2)$, $\upsilon_{sym}(SO_2)$, $\upsilon(NH)$, and $\upsilon(C=N)$ with complex formation showing that SO_2, NH, and C=N were not coordinated in the complexes.

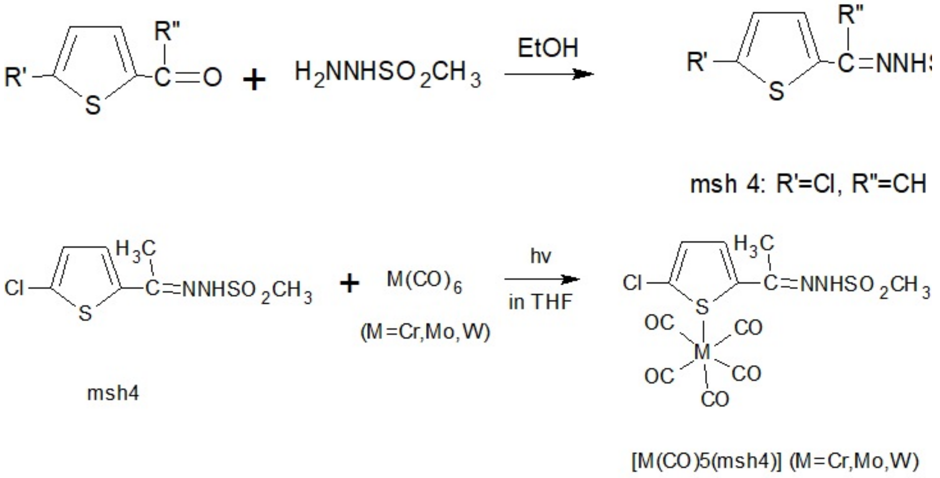

Figure 1. Synthesis of msh 4 and the photochemical reaction of $M(CO)_6(M=Cr,Mo,W)$ with msh 4.

^{1}H spectra in DMSO-d_6 solutions of compounds are reported in the experimental section. In the ^{1}H NMR spectra, an upfield shift of about 0.11 ppm for the ring protons relative to the free ligand was observed. The small shift is related to a decrase in π-electron density in the ring protons with complex formation [33].

The mass spectra show fragmentation via successive loss of CO groups and organic ligands.

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