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Synthesis, Spectroscopic Investigations, Thermal Analysis and DFT Calculations of Some Pentacarbonyl(Mercaptopyrimidine) Metal(0) Complexes of Group VI B Elements

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Abstract: Pentacarbonyl-*N*-mercaptopyrimidinemetal(0) complexes of VIB metals (M: Cr, Mo, W) were formed when hexacarbonylmetal(0) complexes are treated photochemically with 4,6-dimethyl-2-mercaptopyrimidine at 10 ºC. The reported organometallic complexes were purified and isolated under an inert atmosphere. All $M(CO)_5L$ complexes were characterized in solution by FTIR-, ^1H- and ^{13}C-NMR spectroscopies. The FTIR spectroscopy results showed three absorption bands in the carbonyl region which indicates that the pentacarbonyl metal unit of the complexes has a local C_{4v} symmetry. The ^1H- and ^{13}C-NMR spectroscopies showed that the mercaptopyrimidine ligand bonded to the metal complex through the mercaptopyrimidine-nitrogen atom symmetrically. The ^{13}C-NMR spectroscopy results also showed a 1:4 ratio of two peaks in the CO-region, the ratio of the peaks proved the C_{4v} symmetry of these complexes. The thermal behavior of these organometallic complexes is investigated by using DTA/TGA methods. The results of thermal analyses showed that the complexes decomposed at three different temperatures. The density functional theory (DFT) calculations were computed in B3PW91 formalism by Gaussian03W Software. The comparison of the experimental data with the theoretical values showed that the results obtained are compatible with each other. Thus, the accuracy of the experimentally given structural proposal of the obtained organometallic complex compounds was also confirmed through theoretical calculations.

Keywords: Mercaptopyrimidine, Photochemical synthesis, Metal carbonyls, Thermal analysis, DFT

Öz: VIB metallerinin (M: Cr, Mo, W) pentakarbonil-N-merkaptopirimidinmetal(0) kompleksleri, hekzakarbonilmetal(0) kompleksleri 10 ºC'de 4,6-dimetil-2-merkaptopirimidin ligandı ile fotokimyasal olarak sentezlendi. Bildirilen organometalik kompleksler, inert atmosfer altında saflaştırılırlarak izole edilir. Tüm $M(CO)_5L$ kompleksleri çözelti içinde FTIR-, ^1H- ve ^{13}C-NMR spektroskopileri ile karakterize edildi. FTIR spektroskopi sonuçları, karbonil bölgesinde, komplekslerin pentakarbonil metal biriminin yerel bir C_{4v} simetrisine sahip olduğunu gösteren üç absorpsiyon bandı gösterdi. ^1H- ve ^{13}C-NMR spektroskopileri merkaptopirimidin ligandının, merkaptopirimidin-azot atomu yoluyla metal kompleksine simetrik olarak bağlandığını gösterdi. ^{13}C-NMR spektroskopi sonuçları ayrıca CO-bölgesinde 1:4'lük bir oran gösterdi, bu oran komplekslerin C_{4v} simetrisini kanıtladı. Bu organometalik komplekslerin termal davranışı DTA/TGA yöntemleri kullanılarak araştırılmıştır. Termal analizlerin sonuçları, komplekslerin üç farklı sıcaklıkta bozunduğunu göstermiştir. Yoğunluk fonksiyonel teorisi (DFT) hesaplamaları Gaussian03W Software ile B3PW91 formalizmi kullanılarak yapıldı. Deneysel çalışmaların verileri teorik değerlerle karşılaştırıldığında elde edilen sonuçların birbiri ile uyumlu olduğu görülmüştür. Böylece elde edilen organometalik kompleks bileşikleri için deneysel olarak verilen yapısal önermenin doğruluğu teorik olarak da desteklenmiştir.

Anahtar Kelimeler: Merkaptopirimidin, Fotokimyasal sentez, Metal karboniller, Termal analiz, DFT

1. Introduction

As one of the most common π ligands, carbon monoxide plays an essential role in organometallic chemistry due to its ability to coordinate strongly with metals in the zero oxidation state [1-3]. Transition metal carbonyl complexes also have both of industrial and catalytic value and significant structural interest [4, 5] In particular, hexacarbonylmetal(0) complexes of VIB transition metals (Cr, Mo, W) are practical starting materials for many organometallic complex synthesis [6]–[9] since they are air-stable, highly hydrophobic, ready to sublime under vacuum, soluble in polar solvents and very slightly soluble in nonpolar solvents [10]. The photochemical substitution reaction of M(CO)6 complexes is a widely used method to obtain new coordination complexes by releasing carbon monoxide by acceleration of light in photolysis resulting with M(CO)5L type complexes [7]–[9]. The vibrational spectra is very informative and guide the estimation of certain group frequencies in metal carbonyl studies since CO stretching bands in infrared spectra are sharp, environmentally sensitive, and tend to be intense[1]. Metal carbonyl complexes where one or more carbonyl ligand bonded to a single metal center show intense FTIR-bands between 2200 and 1800 cm^{-1} due to the polarization of CO on binding metal atom [11], [12]. The coordination chemistry of heterocyclic ligands is a field of growing interest in coordination chemistry since they have multiple sites, allowing the use of various coordination modes [13]–[16]. Pentacarbonyl(pyridine)metal(0) complexes (M: Cr, Mo, W) have been known for a long time [13]. Since VIB transition metal carbonyls photochemically active, the complexes of these have found to be used in photocatalytic hydrogenation activity [17], CO delivery agent in biochemical and pharmaceutical sources [4,18]. Pyridine has many properties similar to pyrimidine [19], [20] they both act primarily as a σ-donor ligand with weak π-acceptor capacity, the M-N bond in these low-valence metal complexes is not very strong [8]. As one of the main component of nucleic acids, pyrimidines are essential in many biological systems. The coordination chemistry of transition metal complexes containing mercaptopyrimidine ligand are especially interesting. They contain thiolate-S and aromatic-N functional groups that form a variety of complexes with different kind of metals. Additionally, these ligands have the ability to chelate and bind transition metals, providing access to both mononuclear and oligonuclear products [21]–[23]. The ligand 4,6-dimethyl-2-mercaptopyrimidine is an ligand that can coordinate through the S and the pyrimidine ring of N atom [24], [25].

In this study, it was aimed that synthesize and characterize of the pentacarbonyl(primidinethiol)metal(0) complexes of Group VI elements for the first time for this purpose 4,6-dimethyl-2-mercaptopyrimidine (4,6- dimethyl-2-mercaptopyrimidine) ligand was used as mercaptopyrimidine ligand. A useful synthetic technique for producing novel coordination compounds has been the photochemical substitution of ligands, by accelerating with light, most frequently carbonyl groups [6], [8, 9]. For this reason, substituted mercaptopyrimidine ligand photochemically reacted with hexacarbonylmetal(0), M: Cr, Mo, W and resulting complexes were purified by recrystallization. The next part of this work was the structural identification of the synthesized complexes using FTIR-, ^{1}H- and ^{13}C-NMR spectroscopies. Then, by using TGA/DTA methods thermal behavior of the complexes was investigated. Finally, DFT calculations of these organometallic complexes was computed in B3PW91 formalism by Gaussian03W Software.

2. Material and Method

All manipulations, reactions and purification processes were carried out under inert nitrogen atmosphere. Deuterated and analytical grade solvents were purchased from Sigma-Aldrich. Analytical grade solvents were refluxed over metallic sodium for 3-4 days under an inert atmosphere before used. Hexacarbonylchromium(0), hexacarbonylmolibdenum(0), hexacarbonyltungsten(0) and 4,6-dimethyl-2-mercaptopyrimidine were purchased from the Merck GmbH, Darmstadt, Germany, and used without further purification. High pressure mercury lamp (Hg-Tauchlampe TQ 150, Quarzlampen GmbH, Hereaus, Germany, solidex glass, λ>280 nm) was used for photochemical substitution reactions in an immersed apparatus that cooled by circulating water. Photochemical reactions were followed by taking FTIR-spectra from solutions on a Schmadzu FTIR- 8400S spectroscopy. The UV/Vis spectra were recorded from solutions in CH2Cl2 using JASCO V-530 UV/VIS spectrophotometer. The 1H- and ^{13}C-NMR spectra of these complexes were recorded from their dichloroform and d-dimethylsulfoxide solutions using Brucker-Spectroscopin DPX 400 MHz spectrometer. TMS used as an internal reference in all chemical shift values for ^{1}H-, and ^{13}C-NMR. The thermal analyses of the complexes were measured by using SII EXSTAR 6000 TG/DTA6300.

The proposed organometalic complexes have been synthesized using the following reactions where L: 4,6-dimethyl-2-mercaptopyrimidine; M: Cr, Mo, W.

$$M(CO)_6 + THF \xrightarrow{h\upsilon/(-CO)} M(CO)_5(THF) \xrightarrow{h\upsilon/+L} M(CO)_5L + THF$$

0,5 gram $M(CO)_6$ [M: Cr (2,27mmol), Mo (1,89mmol), W (1,42mmol)] was dissolved in THF and illuminated (150 W mercury lamp, λ>280 nm) for 60 minutes at room temperature under oxygen free nitrogen gas. At the of reaction time a stoichiometric amount of 4,6-dimethyl-2-mercaptopyrimidine (0,318g, 0,266g, 0,148g respectively) was added to the reaction vessel and the illumination was kept until the reaction completed (135min. for Cr, 240min. for Mo, 120min. for W). The reaction process was followed by FTIR-spectra taken in every 20 minutes. At the end of the reaction, the color of solutions was yellow for $Cr(CO)_5$(dmmp), red for $W(CO)_5$(dmmp), and dark red for $Mo(CO)_5$(dmmp). Solutions filtered to evacuated schlenk tubes under nitrogen atmosphere. Excess solvents were removed by evaporating under high vacuum. The pure coordination compounds were then isolated by recrystallization from 1:5 mixture CH_2Cl_2 : n-hexane solution producing the solids which were then dissolved in n-hexane to remove out any $M(CO)_6$ remain unreacted. The pure solids were then stored under nitrogen atmosphere at low temperature for analysis.

Spectroscopic Data

Pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)chromium(0) (1)

$Cr(CO)_5$(dmmp); FTIR- (in dichloromethane) ν(CO) (cm^{-1})= 2061.9 (m), 1930.8 (s), 1886.4 (m), ^{1}H-NMR (in d-chloroform) of free ligand δ (ppm)=12.15 (S-H, $H_{(20)}$), 2.33 (CH_3($H_{(22,24)}$-$H_{(26,27)}$), 6.93 ($H_{(18)}$) ref. TMS. ^{1}H-NMR (in d-chloroform) δ (ppm)=13.1 (S-H, $H_{(20)}$), 1.40 (CH_3($H_{(22,24)}$-$H_{(26,27)}$)), 6.70 ($H_{(18)}$) ref. TMS. ^{13}C-NMR (in d-dimethylsulfoxide) of free ligand δ (ppm)= 180 ($C_{(13)}$), 165.1($C_{(14)}$), 111.7 ($C_{(16)}$), 165.1 ($C_{(17)}$), 24.7 ($C_{(21)}$), 24.7 ($C_{(25)}$) ref. TMS. ^{13}C-NMR (in d-dimethylsulfoxide) δ (ppm)= 179.6 ($C_{(13)}$), 168.3($C_{(14)}$), 112.8($C_{(16)}$), 168.3 ($C_{(17)}$), 29.43 ($C_{(21)}$), 28.32 ($C_{(25)}$), 214.9 (Trans-CO), 209.3 (cis-CO) ref. TMS. UV-Vis (in dichloromethane) 243 nm, 2.09557 Abs.

Pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)molybdenum(0) (2)

$Mo(CO)_5(dmmp)$; FTIR- (in dichloromethane) ν(CO) (cm^{-1})= 2061.9 (m), 1932.7(s), 1888.3(m), ^{1}H-NMR (in d-chloroform) of free ligand δ (ppm)=12.15 (S-H, $H_{(20)}$), 2.33 (CH_3($H_{(22,24)}$-$H_{(26,27)}$), 6.93 ($H_{(18)}$) ref. TMS. ^{1}H-NMR (in d-chloroform) δ (ppm)=13.5 (S-H, $H_{(20)}$), 1.38 (CH_3($H_{(22,24)}$-$H_{(26,27)}$), 6.70 ($H_{(18)}$) ref. TMS. ^{13}C-NMR (in d-dimethylsulfoxide) of free ligand δ (ppm)= 180 ($C_{(13)}$), 165.1($C_{(14)}$), 111.7 ($C_{(16)}$), 165.1 ($C_{(17)}$), 24.7 ($C_{(21)}$), 24.7 ($C_{(25)}$) ref. TMS. ^{13}C-NMR (in d-dimethylsulfoxide) δ (ppm)= 181.05 ($C_{(13)}$), 166.03($C_{(14)}$), 109.7($C_{(16)}$), 166.03 ($C_{(17)}$), 30.39 ($C_{(21)}$), 30.39 ($C_{(25)}$), 206.8 (Trans-CO), 200.9 (cis-CO) ref. TMS. UV-Vis (in dichloromethane) 234 nm, 0.8893 Abs., 287nm,1.3061 Abs., 349nm, 0.3203 Abs. and 507nm, 0.1456 Abs.

Pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)tungsten(0) (3)

$W(CO)_5(dmmp)$; FTIR- (in dichloromethane) ν(CO) (cm^{-1})= 2067.7 (m), 1926.6(s), 1891.9(m), ^{1}H-NMR (in d-chloroform) of free ligand δ (ppm)=12.15 (S-H, $H_{(20)}$), 2.33 (CH_3($H_{(22,24)}$-$H_{(26,27)}$), 6.93 ($H_{(18)}$) ref. TMS. ^{1}H-NMR (in d-chloroform) δ (ppm)=12.85 (S-H, $H_{(20)}$), 1.42 (CH_3($H_{(22,24)}$-$H_{(26,27)}$), 6.75 ($H_{(18)}$) ref. TMS. ^{13}C-NMR (in d-dimethylsulfoxide) of free ligand δ (ppm)= 180 ($C_{(13)}$), 165.1($C_{(14)}$), 111.7 ($C_{(16)}$), 165.1 ($C_{(17)}$), 24.7 ($C_{(21)}$), 24.7 ($C_{(25)}$) ref. TMS. ^{13}C-NMR (in d-dimethylsulfoxide) δ (ppm)= 180.8 ($C_{(13)}$), 165.6($C_{(14)}$), 111.71($C_{(16)}$), 166.0 ($C_{(17)}$), 30.32 ($C_{(21)}$), 30.32 ($C_{(25)}$), 198.2 (Trans-CO), 190.6 (cis-CO) ref. TMS. UV-Vis (in dichloromethane) 243nm, 2.04778 Abs., 294nm, 0.5262 Abs. and 352nm, 0.3904 Abs

3. Result and Discussion

Photolysis of hexacarbonylmetal(0) complexes of VIB transition metals in the presence of an excess amount of tetrahydrofuran (THF) leads to the formation of pentacarbonyl(THF)metal(0), $M(CO)_5(THF)$ intermediate compound. UV-irradiation with 4,6-dimethyl-2-mercaptopyrimidine of the intermediate pentacarbonyl complex leads to the formation of pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)metal(0); M: Cr, Mo, W complexes. The photochemical substitution reactions were followed by IR spectra. It was seen that the absorption band at 1980 cm^{-1} which is specific to $M(CO)_6$ υ(CO) band decreases while three new distinct bands occurred with proceeding of the photochemical reaction.

The FTIR spectra of $M(CO)_5L$ (L:4,6-dimethyl-2-mercaptopyrimidine) in dichloromethane exhibits three prominent absorption bands (one in strong, the others in medium intensities) in the CO stretching vibrational region (1800–2300 cm^{-1}). The three-band ν(CO) pattern of these complexes indicates that the C4v local symmetry of $M(CO)_5$ skeleton, which is generally observed for $M(CO)_5L$ complexes with a pattern $2A_1$+E [5]. The A1 and E modes are both IR-active modes where E must be lower in frequency than one of A1- modes as explained by Orgel [26].

The ^{1}H-NMR spectrum of free 4,6-dimethyl-2-mercaptopyrimidine ligand shows three singlets with different intensities at 2.33, 6.93 and 12.15 ppm. Upon coordination to the metal atom the signal due to the SH group show no significant shift from that of free ligands. The appearance of only one singlet for the SH group proton which show no shift from that of the free ligand could rule out any metalsulfure coordination. The appearance of only one singlet for the CH_3 groups with no significant chemical shift in an indication of the metal-nitrogen coordination through the nitrogen lone pair of the pyrimidine ring. From these 1H-NMR and previous IR-data discussed, the can conclude the appearance of metal-pyrimidine coordination through the nitrogen atom lone pair of the pyrimidine ring rather than the expected metal-thiol coordination.

The 13C-NMR spectra of the complexes M(CO)5(4,6-dimethyl-2- mercaptopyrimidine); M: Cr, W were recorded from their d-chloroform solutions, M: Mo recorded from its d-dimethylsulfoxide solution. The ^{13}C-NMR spectra show four signals in the region of 20-180 ppm for the pyrimidine ring and its substituents. The carbonyl groups give two signals 37 with relative intensities 1:4 in the region of 190-230 ppm. The ^{13}C-{1H}-NMR spectrum of the free 4,6-dimethyl-2-mercaptopyrimidine ligand (dmmp) show four signals with relative intensities at 179.9, 169, 118.7 and 23.8 ppm. Upon coordination to the metal atom, the signal belongs to C(13) show no significant shift comparing with that of free ligand. From the 13C-NMR data of the complexes one can said that (i) The appearance of only one singlet for all the carbons of the pyrimidine ring an indication for the symmetric metal-ligand coordination through on of the ring nitrogen atoms, (ii) All the 13C-signals of all carbons of the pyrimidine ring and substituents show no significant shift from these of free ligands indicates weak metal-nitrogen coordination, (iii) The appearance of two signals of relative intensities 1:4 in the CO region indicates the formation of pentacarbonylmetal, $M(CO)_5$.

The thermal analysis of the complexes M(CO)5L (M: Cr, W ; L: 4,6-dimethyl-2-mercaptopyrimidine) was measured by using TG/DTA method. $Cr(CO)_5(dmmp)$ complex dissociates at four different temperatures, in order of 105.9 °C , 214.9 °C , 452.7 °C and 890.2 °C. It can be postulated that the complex Cr(CO)5(4,6-dm-2-mp) was dissociated to CrO_3. $Mo(CO)_5(dmmp)$ complex (2) dissociates at five different temperatures, in order of 59.7 °C, 119.8 °C, 169.7 °C, 370.2 °C and 900.9 °C and the main dissociation of the complex is occurred at 160 °C. Thermal dissociations of the complexes were given in Table 1 and Table 2.

Table 1. Thermal dissociation of $Cr(CO)_5$(dmmp) complex

Decomposition Steps	Sample Amount *(mg)*	Lost Amount *%*	Lost Molecular Weight *(g/mol)*
1st	1,873	7%	21,247
2nd	1,468	19,33%	64
3rd	0,932	50,24%	166,38
4th	0,631	66,31%	219,59

Table 2. Thermal dissociation of $Cr(CO)_5$(dmmp) complex

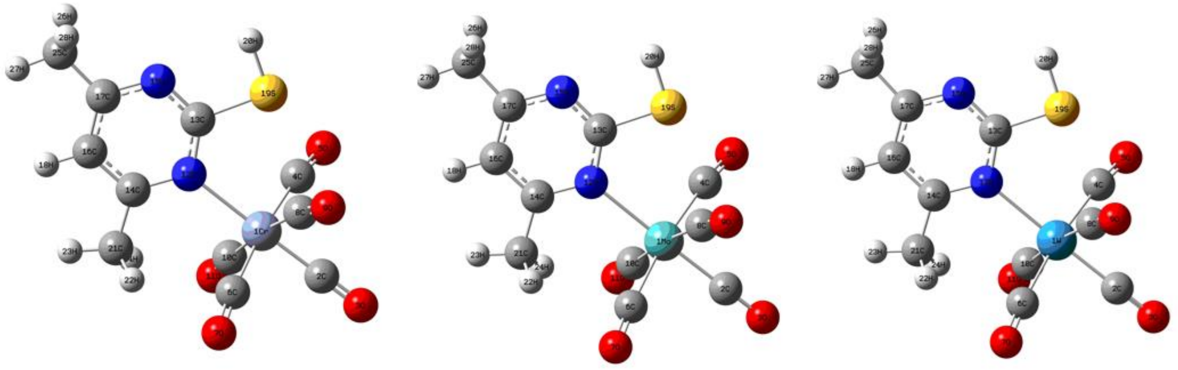
Decomposition Steps	Sample Amount *(mg)*	Lost Amount *%*	Lost Molecular Weight *(g/mol)*
1st	4,613	2,60%	9,78
2nd	4,493	17,58%	66,13
3rd	3,802	41,45%	155,9
4th	2,387	48,25%	181,52

4. Computational Details

The optimized molecular structure, bond distances and bond angles of the pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)metal(0); M: Cr, Mo, W complexes have been computed by using DFT-B3PW91formalism. Optimized geometry of M(CO)5(dmmp) complex is given in Figure 2 with atom labels, grey atoms represent hydrogen, dark grey atoms represent carbon, blue atoms represent nitrogen, yellow atom represents sulphur, turquoise atom represents metal, and red atoms represent oxygen. Bond distances between atoms and bond angles between selected atoms were given in Table 3 and Table 4.

Table 3. DFT (B3PW91/SDD) Calculated bond distances between atoms

Atoms	$Cr(CO)_5$(dmmp)	$Mo(CO)_5$(dmmp)	$W(CO)_5$(dmmp)
$M_{(1)}$ - $C_{(2)}$	1,8264	1,9691	1,9852
$M_{(1)}$ - $C_{(4)}$	1,8892	2,045	2,0541
$M_{(1)}$ - $C_{(6)}$	1,8649	2,0232	2,034
$M_{(1)}$ - $C_{(8)}$	1,8893	2,0448	2,0539
$M_{(1)}$ - $C_{(10)}$	1,8647	2,024	2,0351
$M_{(1)}$ - $N_{(12)}$	2,2434	2,3667	2,3509
$C_{(2)}$ - $O_{(3)}$	1,1832	1,1845	1,1857
$C_{(4)}$ - $O_{(5)}$	1,1766	1,1775	1,1789
$C_{(6)}$ - $O_{(7)}$	1,1811	1,1818	1,1834
$C_{(8)}$ - $O_{(9)}$	1,1765	1,1772	1,1786
$C_{(10)}$ - $O_{(11)}$	1,181	1,1817	1,1832
$N_{(12)}$ - $C_{(13)}$	1,3746	1,3739	1,377
$N_{(12)}$ - $C_{(14)}$	1,3842	1,3827	1,3847
$C_{(13)}$ - $N_{(15)}$	1,3447	1,3437	1,3425
$C_{(13)}$ - $S_{(19)}$	1,8034	1,8017	1,801
$C_{(14)}$ - $C_{(16)}$	1,4054	1,4044	1,4038
$C_{(14)}$ - $C_{(21)}$	1,5013	1,4993	1,499
$N_{(15)}$ - $C_{(17)}$	1,3527	1,3538	1,3537
$C_{(16)}$ - $C_{(17)}$	1,4008	1,4017	1,4015
$C_{(16)}$ - $H_{(18)}$	1,0828	1,0829	1,0828
$C_{(17)}$ - $C_{(25)}$	1,4994	1,4994	1,4991
$S_{(19)}$ - $H_{(20)}$	1,3741	1,3747	1,3752
$C_{(21)}$ - $H_{(22)}$	1,0922	1,0949	1,0949
$C_{(21)}$ - $H_{(23)}$	1,0932	1,0932	1,0932
$C_{(21)}$ - $H_{(24)}$	1,092	1,0911	1,0913
$C_{(25)}$ - $H_{(26)}$	1,096	1,0961	1,0962
$C_{(25)}$ - $H_{(27)}$	1,093	1,0931	1,093
$C_{(25)}$ - $H_{(28)}$	1,0959	1,0959	1,0959



(a) **(b)** **(c)**

Figure 1. The optimized structure of $M(CO)_5(dmmp)$ complexes,; a) Cr, b) Mo, c) W.

Table 4. DFT (B3PW91/SDD) Calculated bond angles between atoms

Atoms	**$Cr(CO)_5(dmmp)$**	**$Mo(CO)_5(dmmp)$**	**$W(CO)_5(dmmp)$**
$C_{(2)}$-$M_{(1)}$-$C_{(4)}$	85,99	85,82	85,84
$C_{(2)}$ - $M_{(1)}$ - $C_{(6)}$	86,6	86,21	86,2
$C_{(2)}$ - $M_{(1)}$ - $C_{(8)}$	86,17	86,63	86,59
$C_{(2)}$ - $M_{(1)}$ -$C_{(10)}$	86,8	87,05	86,99
$C_{(4)}$ - $M_{(1)}$ - $C_{(8)}$	95,01	94,36	94,41
$C_{(4)}$ - $M_{(1)}$ -$C_{(10)}$	86,29	86,19	86,23
$C_{(4)}$ - $M_{(1)}$ -$C_{(12)}$	93,01	93,19	93,13
$C_{(6)}$ - $M_{(1)}$ - $C_{(8)}$	86,33	86,92	86,96
$C_{(6)}$ - $M_{(1)}$ -$C_{(10)}$	91,46	91,65	91,51
$C_{(6)}$ - $M_{(1)}$ -$C_{(12)}$	94,42	94,8	94,86
$C_{(8)}$ - $M_{(1)}$ -$C_{(12)}$	93,09	92,6	92,53
$C_{(10)}$ -$M_{(1)}$-$C_{(12)}$	93,98	93,73	93,91
$M_{(1)}$- $N_{(12)}$-$C_{(13)}$	121,07	121,19	121,31
$M_{(1)}$- $N_{(12)}$-$C_{(14)}$	124,28	123,8	123,77
$C_{(13)}$-$N_{(12)}$- $C_{(14)}$	114,65	114,97	114,9
$N_{(12)}$-$C_{(13)}$ -$N_{(15)}$	126,52	126,35	126,26
$N_{(12)}$ - $C_{(13)}$-$S_{(19)}$	119,86	119,3	119,39
$N_{(15)}$ - $C_{(13)}$-$S_{(19)}$	113,62	114,36	114,36
$N_{(12)}$- $C_{(14)}$-$C_{(16)}$	120,95	120,85	120,83
$N_{(12)}$ -$C_{(14)}$-$C_{(21)}$	121,78	121,06	121,19
$C_{(16)}$ -$C_{(14)}$-$C_{(21)}$	117,27	118,09	117,98
$C_{(13)}$ -$N_{(15)}$-$C_{(17)}$	118,95	118,85	119,02
$C_{(14)}$ -$C_{(16)}$-$C_{(17)}$	120,05	119,9	120,01
$C_{(14)}$ -$C_{(16)}$-$H_{(18)}$	119,42	119,52	119,42
$C_{(17)}$-$C_{(16)}$ -$H_{(18)}$	120,53	120,58	120,57
$N_{(15)}$ -$C_{(17)}$-$C_{(16)}$	118,87	119,06	118,97
$N_{(15)}$ -$C_{(17)}$-$C_{(25)}$	117,35	117,28	117,3
$C_{(16)}$ -$C_{(17)}$-$C_{(25)}$	123,77	123,67	123,73
$C_{(13)}$ -$S_{(19)}$-$H_{(20)}$	92,97	93,03	92,91
$C_{(14)}$-$C_{(21)}$- $H_{(22)}$	111,78	110,75	110,86
$C_{(14)}$-$C_{(21)}$- $H_{(23)}$	109,61	110,02	109,93
$C_{(14)}$-$C_{(21)}$- $H_{(24)}$	112,02	112,13	112,17
$H_{(22)}$-$C_{(21)}$- $H_{(23)}$	107,72	107,91	107,9
$H_{(22)}$ -$C_{(21)}$-$H_{(24)}$	107,79	107,43	107,42
$H_{(23)}$-$C_{(21)}$- $H_{(24)}$	107,73	108,45	108,41
$C_{(17)}$-$C_{(25)}$- $H_{(26)}$	109,98	109,96	109,96
$C_{(17)}$-$C_{(25)}$- $H_{(27)}$	111,85	111,85	111,86
$C_{(17)}$-$C_{(25)}$- $H_{(28)}$	110,01	110,03	110,03
$H_{(26)}$-$C_{(25)}$- $H_{(27)}$	108,94	108,92	108,92
$H_{(26)}$-$C_{(25)}$- $H_{(28)}$	106,94	106,94	106,92
$H_{(27)}$-$C_{(25)}$- $H_{(28)}$	108,99	109,01	109,02

The vibrational frequencies, the nuclear magnetic resonance chemical shift values and energies of the pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)metal(0); M: Cr, Mo, W complexes have been computed by using DFT-B3PW91 with SDD. The comparison table of the FTIR spectra of the complexes and DFT calculated stretching bands of the complexes is given in Table 5. Calculated NMR chemical shifts of the complexes were given in Table 6.

Table 5. Experimental and DFT (B3PW91/SDD) Calculated vibrational streching frequencies of M(CO)$_5$(dmmp) complexes

Vibration	**Cr(CO)$_5$(dmmp)**		**Mo(CO)$_5$(dmmp)**		**W(CO)$_5$(dmmp)**	
	Experimental *(cm^{-1})*	**Theoretical *(cm^{-1})***	**Experimental *(cm^{-1})***	**Theoretical *(cm^{-1})***	**Experimental *(cm^{-1})***	**Theoretical *(cm^{-1})***
υ(CO)	2061,9	2036,06	2061,97	2036,68	2034,12	2067,5
υ(CO)	1930,81	1925,7	1932,74	1917,33	1926,56	1913,3
υ(CO)	1886,44	1914,3	1888,37	1905,8	1891,88	1900,18
υ(C=C)Aromatic	1604,83	1633,76	1653,49	1634,07	1653,05	1635,43
υ(C=C)Aromatic	1535,39	1565,4	1558,91	1564,48	1558,5	1563,2
υ(M-N)	420,5	419,36	418,51	397,01	418,5	402,55
υ(C-C)	1429,3	1449,57	1437,21	1449,52	1431,23	1449,74
υ(C-C)	1425,44	1451,6	1429,46	1450,58	1454,38	1451,09
υ(CH$_3$)	3064,99	3097,37	3080,37	3087,32	3078,44	3087,46
υ(CH$_3$)	3053,42	3070,74	3074,61	3070,68	3068,5	3070,69
υ(C-N)	1290,42	1303,74	1290,71	1306,96	1292,5	1309,34
υ(C=N)	1411,94	1400,09	1244,48	1238,5	1242,2	1236,74
υ(C-H) Bend	794,7	795,01	889,23	794,98	794,81	794,35
υ(C-H) Bend	893,07	896,96	901,02	894,67	906,41	895,68
υ(C-S)	889,21	879,66	893,27	880,93	889,31	879,55

Table 6. Experimental and DFT-Calculated NMR chemical shifts (ppm) of M(CO)$_5$(dmmp) complexes, TMS reference.

δ (ppm)	**Free Ligand**	**Cr(CO)$_5$(dmmp)**		**Mo(CO)$_5$(dmmp)**		**W(CO)$_5$(dmmp)**	
		Experimental	**DFT-B3PW91**	**Experimental**	**DFT-B3PW91**	**Experimental**	**DFT-B3PW91**
S-H, H$_{(20)}$	12.15	13.1	4.93	13.5	4.82	12.85	4.82
CH$_3$(H$_{(22,24)}$-H$_{(26,27)}$	2.33	1.40	1.82	1.38	1.78	1.42	1.77
H$_{(18)}$	6.93	6.70	6.33	6.70	6.33	6.75	6.28
C$_{(13)}$	179.9	179.6	182.04	181.05	180.6	180.8	180.68
C$_{(14)}$	169.0	168.3	165.7	166.03	164.18	165.6	164.1
C$_{(16)}$	118.7	112.8	106.9	109.7	106.07	111.71	106.1
C$_{(17)}$	169.0	168.3	157.13	166.03	157.53	166.0	157.07
C$_{(21)}$	23.8	29.43	15.69	30.39	15.81	30.32	15.69
C$_{(25)}$	23.8	28.32	21.7	30.39	21.93	30.32	15.8
trans-CO		214.9	225.4	206.8	225.4	198.2	216.78
cis-CO		209.3	218.9	200.9	215.3	190.6	208.38

The HOMO-LUMO transition energies of the complexes was calculated by Gaussian molecular visualization program by using DFT-B3PW91 method as shown in Figure 3. HOMO electrons mostly occupied on mercaptopyrimidine ligand part while LUMO electrons localized on pentacarbonyl metal moiety of the complex. Electronic transition calculations of pentacarbonyl(mercaptoyrimidine)metal(0) complexes were carried out by DFT-B3PW91/SDD formalism (Table 7). Thermodynamic energy term table is given in Table 8.

Table 7. DFT (B3PW91/SDD) Calculated electronic transitions of M(CO)$_5$(dmmp) complexes

Exited States	**Cr(CO)$_5$(dmmp)**			**Mo(CO)$_5$(dmmp)**			**W(CO)$_5$(dmmp)**		
	λ *(nm)*	**E** *(eV)*	**f**	**λ** *(nm)*	**E** *(eV)*	**f**	**λ** *(nm)*	**E** *(eV)*	**f**
H - 2 → L + 4	397,2	3,1214	0,0172	386,9	3,2048	0,0154	403,4	3,0738	0,0153
H - 2 → L + 3	389,6	3,1822	0,0124	382,4	3,2424	0,0177	397,9	3,1158	0,016
H → L	384,7	3,2226	0,0006	399,6	3,1029	0,0011	421	2,9451	0,0004
H - 2 → L + 1	372,6	3,3279	0,003	373,1	3,3233	0,0467	388,7	3,1894	0,0669

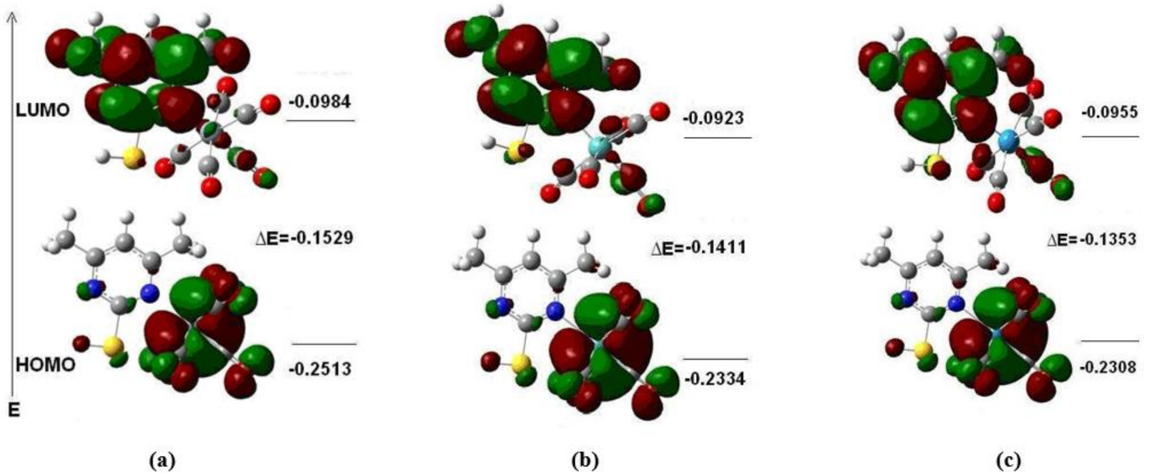


Figure 2. The electronic transition from HOMO to LUMO of the $M(CO)_5$(dmmp) complexes; (a) $Cr(CO)_5$(dmmp), (b) $Mo(CO)_5$(dmmp), (c) $W(CO)_5$(dmmp)

Table 8. DFT (B3PW91/SDD) Calculated thermodynamic properties of $M(CO)_5$(dmmp) complexes

Thermodynamic Properties	Cr	Mo	W
Total Energy (a.u.)	-1394,203	-1375,5869	-1374,4947
Zero-Point Energy (KCal/Mol)	110,1081	109,0723	109,0984
Rotational Constants (GHZ)	0,4306 0,2339 0,2017	0,3995 0,213 0,1861	0,397 0,2063 0,1807
Rotational Temperatures (K)	0,0207 0,0112 0,0097	0,0192 0,0102 0,0089	0,0191 0,0099 0,0087
Dipole Moment (Debye)	9,0125	9,3578	9,7212
RMS Gradient Norm (a.u.)	1,86E-06	1,508E-05	6,74E-06
Virial Ratio (a.u.)	2,0361	2,0381	2,0375
Entropy (Cal/Mol-Kelvin)			
Total	161,66	162,36	162,524
Translational	43,295	43,681	44,293
Rotational	34,025	34,273	34,34
Vibrational	84,341	84,406	83,892
Thermal Energy (KCal/Mol)			
Total	123,809	123,102	123,087
Translational	0,889	0,889	0,889
Rotational	0,889	0,889	0,889
Vibrational	122,031	121,325	121,309

Reliable molecular structure prediction is one of the main goals of computational chemistry. According to the bond length and vibrational calculation data collected by DFT (B3PW91/SDD) of these synthesized organometallic complexes, the mercaptopyrimidine ligand is attached to the central atom through nitrogen atom, rather than the expected metal-thiol coordination. DFT calculations of ^{1}H- and ^{13}C- chemical shifts of the complexes and free ligand are compared to experimental results also shows bonding through pyrimidine nitrogen atom with C_{4v} symmetry. Accurate thermochemical data for each metal-ligand bond strength is crucial for the rational design of catalytic processes. Calculated thermodynamic properties of pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)metal(0); M: Cr, Mo, W complexes are important in terms of directing further catalytic studies.

5. Conclusions

The In this study, pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)metal(0); M: Cr, Mo, W complexes were photochemically synthesized, and their structures have been characterized by the mean of IR-, UV-, ^{1}H-NMR and ^{13}C-NMR spectroscopies and their thermal behavior investigate by TG/DTA methods. The ligand 4,6-dimethyl-2-

mercaptopyrimidine is chosen because of its multifunctional groups and multibonding probability. There are three basic centers in the ligand that are available to bond lewis acid (metal center). The most basic center is that N atom due to the spectroscopic investigations so the central atom is bonded to ligand from N atom of mercaptopyrimidine. Despite the fact that the CO group is the strongest - acceptor ligand, the bond lengths have changed, making the M-C bond weaker and, of course, creating a synergistic energy in the M-CO bond. The ^{1}H- and ^{13}C-NMR spectroscopies showed that the mercaptopyrimidine ligand bonded to metal complex through the mercaptopyrimidine nitrogen atom symmetrically. Also, the ^{13}C-NMR spectroscopy results showed 1:4 ratio of peaks in the CO-region, the ratio of the peaks proved the C_{4v} symmetry of these complexes. In addition to experimental studies, the complexes of pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)metal(0) were investigated theoretically by DFT computational method. After geometry optimizations, vibrational frequencies computed by calculating the 47 harmonic vibrational frequencies of complexes and compared with experimental spectra of the complexes. It was seen that vibrational spectra values were in a good aggrement with experimental data. Also DFT calculated proton shifts compared with both free ligand and experimental results confirmed that there is an successful application of DFT to proton chemical shifts.

Competing Interest / Conflict of Interest

The authors declare that they have no competing interests.

Author Contribution

We declare that all Authors equally contribute.

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