

*Full Length Research Paper*

# “Photochemical synthesis and spectroscopic studies of 3, 5-alkyl/aryl substituted-tetrahydro-2H-1,3,5-thiadiazine-2-thione and their complexes with $M(CO)_4(\eta^{2:2}\text{-NBD})$ [M = Cr, Mo and W] as $M(CO)_4$ transfer reagent”

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Fifteen new complexes,  $[M(CO)_4(L)2]$  [M=Cr; Mo; W]; [L= met-DTTT; et-DTTT; n-pr-DTTT; ph-DTTT and benz-DTTT] have been synthesized by the photochemical exchange reaction of  $[(\eta^{2:2}\text{-NBD})M(CO)_4]$  (M=Cr, Mo and W) with 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (met-DTTT), 3,5-diethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (eth-DTTT), 3,5-di-n-propyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (n-pr-DTTT), 3,5-diphenyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (ph-DTTT), and 3,5-dibenzyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (benz-DTTT). The new complexes have been characterized by elemental analysis, FTIR, <sup>1</sup>H NMR spectroscopy. The spectroscopic studies show that DTTT behaves as a monodentate ligand coordinating via the sulfur (C=S) donor atom.

**Key words:** Metal carbonyl, 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione, exchange reactions.

## INTRODUCTION

Dazomet (3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione or met-DTTT) is the fumigant or pesticide currently used to control soil fungi in both the conifer and shrub seedbeds. Control of soil-borne fungi, especially those which cause damping-off, has been good (Goksoyr, 1964). Soil fumigants are pesticides that form gases when applied to soil. Once in the soil, the fumigants work by controlling pests that can disrupt plant growth and crop production. Soil fumigants play a very important role in agriculture, but they also have the potential to pose risk concerns to people (like handlers, workers and bystanders). Soil fumigation can provide benefits to both food consumers and growers. The magnitude of benefits depends on pest pressure, which varies over space and time, and the availability and costs associated with the use of alternatives (Reregistration Eligibility Decision for Dazomet, 2008).

Dazomet is applied before the planting of crops by soil incorporation, thereby causing it to act as a soil fumigant and disinfectant by decomposing to methyl isothiocyanate. It controls soil fungi (such as, Fusarium, Pythium, Rhizoctonia, Sclerotinia, Verticillium and Colletotrichum coch2:2-NBDes atramentarium), nematodes, germinating weed seeds and soil-dwelling insects (The Pesticide Manual, 2000).

In agriculture, DTTT has found application as fungicide, herbicide and nematocide for cabbage, cucumber, maize, potato and tomato plants. In industrial environments, DTTT has been used as slimicide in paper mills, as a biocide in metal working fluids used in the manufacture of engines, transmissions, aircraft and especially metal products. The chemical DTTT has also been considered for use as a biocide in pump spray-delivered consumer products and custodial supplies. Respiratory exposure may occur from liquid aerosol generated during spray application of materials containing DTTT. Perhaps of a greater significance is the potential for exposure to volatile and semivolatile degradation products of DTTT.

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This 'CS<sub>2</sub>' incorporated heterocycle is sparingly soluble in water and it has been equivocally proposed to undergo decomposition to formaldehyde, methylisothiocyanate and other compounds in aqueous solution (Drescher and Otto, 1968; Munnecke et al., 1962; Munnecke, 1963; Syamsunder, 1964; Buu-Hoi and Xoung, 1958; Shankarwar et al., 2008; Srivastava and Shrimal, 2002; Subasi et al., 2006; Chakraborty and Patel, 1996; Amar et al., 2002). It has been reported that DTTT gave unstable complexes with Cu(II), Co(II), Ni(II), Fe(III) ions in solution and were not isolated in solid form (Klement et al., 1999). Sulfide carbonyl compounds continue to attract considerable attention not only on account of their fascinating structural chemistry, but also because of their ability to act as electron reservoirs and their potential in catalysis (Martell, 1987). Features of the chemistry of these molecules which are currently of interest include the mechanisms and sites of substitution as well as the modification of reactivity accompanying carbonyl replacement by donor ligands (Zhao et al., 2001). Complexes [M(CO)<sub>5</sub>(DTTT)] [M=Cr, Mo, W], Re(CO)<sub>4</sub>Br(DTTT) and [Mn(CO)<sub>2</sub>Cp(DTTT)] have been reported (Sema et al., 2003). NBD ( $\eta^{2,2}$ -norbornadiene) forms organometallic complexes, where it can act as a two-electron or four-electron donor. Sandwiched compounds such as tetracarbonyl ( $\eta^{2,2}$ -norbornadiene) chromium (0), which is a useful reagent for transferring chromium tetracarbonyl to bidentate phosphine ligands, are known (Markus et al., 2004). 1,5-cyclooctadiene is also the starting material for the synthesis of diamantene and sumanene and it is used as an acetylene transfer agent for instance in reaction with 3,6-di-2-pyridyl-1,2,4,5-tetrazine (Ronald et al., 2001). The thermal substitution of Mo(CO)<sub>4</sub>( $\eta^{2,2}$ -COD) and Mo(CO)<sub>4</sub>( $\eta^{2,2}$ -NBD) with, BFEDA gave the same product which was isolated by using the same procedure. Thus, both Mo(CO)<sub>4</sub>( $\eta^{2,2}$ -NBD) and Mo(CO)<sub>4</sub>( $\eta^{2,2}$ -COD) can be used as Mo(CO)<sub>4</sub> transfer reagent for the synthesis of Mo(CO)<sub>4</sub>(BFEDA) (Fatma S.K., 2005; Ayodhya et al., 2010). These literatures prompted us to study the behavior of ( $\eta^{2,2}$ -NBD)M(CO)<sub>4</sub> as transfer reagent in G-6 metal carbonyl complexes.

In this paper, we have used five Schiff bases (Scheme 1) namely 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (met-DTTT), 3,5-diethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (eth-DTTT), 3,5-di-n-propyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (n-pr-DTTT), 3,5-diphenyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (ph-DTTT), 3,5-dibenzyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (benz-DTTT) as ligands with M(CO)<sub>4</sub>( $\eta^{2,2}$ -NBD) (where M=Cr, Mo and W). M(CO)<sub>4</sub>( $\eta^{2,2}$ -NBD) was utilized as M(CO)<sub>4</sub> transfer reagent.

In this paper, we report a noble photochemical route to the hitherto unknown fifteen new complexes (1a to 3e). The complexes were characterized by elemental analysis, FT-IR, 1H-NMR spectroscopy. According to this, the ligands (a to e) coordinates to the metal via (C=S) sulfur donor atom in (1a to 3e). The spectroscopic studies suggest monodentate coordination of ligands in

{M(CO)<sub>4</sub>(met-DTTT)<sub>2</sub>} (1a to 3a); {M(CO)<sub>4</sub>(eth-DTTT)<sub>2</sub>} (1b to 3b); {M(CO)<sub>4</sub>(n-pr-DTTT)<sub>2</sub>} (1c to 3c); {M(CO)<sub>4</sub>(ph-DTTT)<sub>2</sub>} (1d to 3d) and {M(CO)<sub>4</sub>(benz-DTTT)<sub>2</sub>} (1e to 3e); where (M=Cr, Mo and W).

## MATERIALS AND METHODS

Reactions were carried out under dry argon or in vacuo. All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer (Model-577) in KBr discs and CH<sub>2</sub>Cl<sub>2</sub>. All the melting points were determined in an open capillary and are uncorrected. All glassware was oven dried at 120°C, molecular weight of the complexes was determined cryoscopically in benzene. Dichloromethane, 2,5-norbornadiene ( $\eta^{2,2}$ -NBD), n-hexane, n-pentane, benzene, methyl amine hydrochloride, formaldehyde, carbon disulfide, triethyl amine and iso-octane were purchased from E. Merck, while M(CO)<sub>6</sub> (M = Cr, Mo, W), 3,5-diethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (eth-DTTT), 3,5-di-n-propyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (n-pr-DTTT), 3,5-diphenyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (ph-DTTT), 3,5-dibenzyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (benz-DTTT) were purchased from Aldrich and were used as supplied.

Magnetic susceptibility measurements of the complexes were carried out by Gouy method. UV irradiation was performed with a medium pressure 400W mercury lamp through a quartz bulb.

Synthesis of the 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (met-DTTT). The 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (met-DTTT) was prepared as described in the literature (Wing-Wah et al., 1993). A solution of CH<sub>3</sub>NH<sub>2</sub>.HCl (5.0 g, 73 mmol) in water (6 ml) and triethylamine (8.62 g, 86 mmol) was stirred for 10 min, and then CS<sub>2</sub> (2.84 g, 38 mmol) was added drop wise at room temperature with stirring for 20 min. Formaldehyde (2.30 g, 76 mmol) was added drop wise to the above reaction mixture, which was stirred for 30 min until a white precipitate was formed. met-DTTT was obtained as white solid by filtration with 80% yield. The complex was characterized and identified by means of IR and 1H-NMR spectroscopy. IR (in CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\text{sym}}$  (C=S) 655 cm<sup>-1</sup>,  $\nu_{\text{as}}$  (C=S) 600 cm<sup>-1</sup>, 1H-NMR (in CDCl<sub>3</sub>)  $\delta$ = 2.46 (s, 3H, 5-CH<sub>3</sub>), 3.30 (s, 3H, 3-CH<sub>3</sub>), 1.27 (s, 2H, 2-CH<sub>2</sub>), 4.34 (s, 2H, 4-CH<sub>2</sub>).

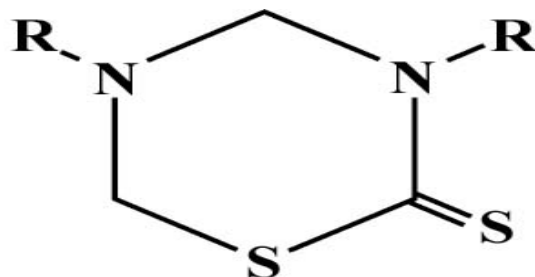
### Synthesis of the Mo(CO)<sub>4</sub>(bicyclo[2.1.1] hepta-2,5-diene) or Mo(CO)<sub>4</sub>( $\eta^{2,2}$ -NBD)

Mo(CO)<sub>4</sub>( $\eta^{2,2}$ -NBD), Cr(CO)<sub>4</sub>( $\eta^{2,2}$ -NBD) and W(CO)<sub>4</sub>( $\eta^{2,2}$ -NBD) were prepared following the method described in the literature (King, 1965; King, 1963, Sarikahya and Senturk, 2001, Warner H. Prinz R., 1965). The preparation of Tetracarbonyl ( $\eta^{2,2}$ -NBD) molybdenum(0) is typical and is given here.

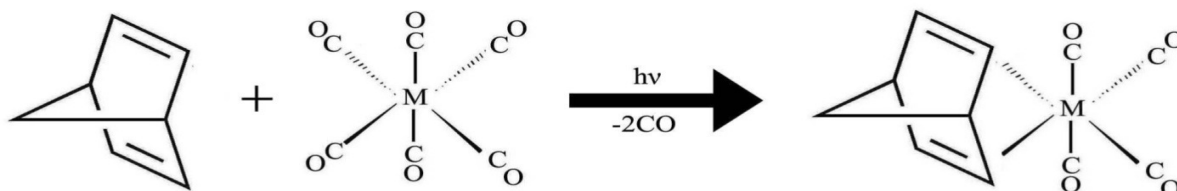
Tetracarbonyl ( $\eta^{2,2}$ -NBD)molybdenum(0), was prepared by refluxing Mo(CO)<sub>6</sub> and 2,5-norbornadiene ( $\eta^{2,2}$ -NBD) in iso-octane. The reaction solution was evaporated to dryness. Crystallization from n-hexane solution yields yellow crystals of the complex. The solvent was decanted and crystals were dried in vacuum. The complex was characterized and identified by means of IR spectroscopy. IR (in toluene): A<sub>1</sub>(2)=2038, A<sub>1</sub>(1), B<sub>1</sub>= 1948, B<sub>2</sub>=1885 cm<sup>-1</sup>. Mo(CO)<sub>4</sub>( $\eta^{2,2}$ -NBD) was obtained in 75% yield.

### Preparation of (met-DTTT)<sub>2</sub>Mo(CO)<sub>4</sub> complex from exchange reaction of [( $\eta^{2,2}$ -NBD)Mo(CO)<sub>4</sub>]

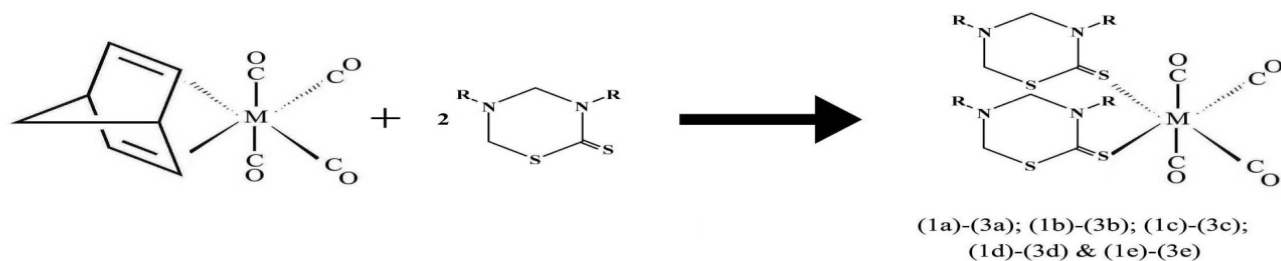
0.45 g (1.5 mmol) sample of norbornadienetetracarbonylmolybdenum [( $\eta^{2,2}$ -NBD)Mo(CO)<sub>4</sub>] was dissolved in 25 ml of n-pentane. Then 0.486 g (3 mmol) of met-



**Scheme 1.** a. (met-DTTT; R=CH<sub>3</sub>); b. (eth-DTTT; R=C<sub>2</sub>H<sub>5</sub>); c. (n-pr-DTTT; R=C<sub>3</sub>H<sub>7</sub>); d. (ph-DTTT; R=C<sub>6</sub>H<sub>5</sub>) and e. (benz-DTTT; R=C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>).



**Scheme 2.** Thermal reaction of  $\eta^{2:2}$ -NBD with  $M(\text{CO})_6$  (M = Cr, Mo, W).



**Scheme 3.** Ligand Substitution reaction of  $\eta^{2:2}$ -NBD in  $M(\text{CO})_4(\eta^{2:2}\text{-NBD})$  with DTTT. (1): M=Cr; (2): M=Mo; (3): M=W; (a): met-DTTT, R=CH<sub>3</sub>; (b): eth-DTTT, R=C<sub>2</sub>H<sub>5</sub>; (c): n-Pr-DTTT, R=C<sub>3</sub>H<sub>7</sub>; (d): ph-DTTT, R=C<sub>6</sub>H<sub>5</sub> and (e): benz-DTTT, R=C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>.

DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any  $[(\eta^{2:2}\text{-NBD})M(\text{CO})_4]$ ,  $\eta^{2:2}$ -NBD ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH<sub>2</sub>Cl<sub>2</sub>/n-hexane solution for recrystallization. Yellow microcrystal of  $[\text{Mo}(\text{CO})_4(\text{met-DTTT})_2]$  were obtained after waiting 24 h at -15°C with 71% yield.

The other 14 complexes were prepared according to same procedure as described for the preparation of afore mentioned complex by using appropriate  $[(\eta^{2:2}\text{-NBD})M(\text{CO})_4]$  (M= Cr, Mo and W) and (met-DTTT), (eth-DTTT), (n-pr-DTTT), (ph-DTTT) and (benz-DTTT).

## RESULTS AND DISCUSSION

The transfer reagents  $\text{Mo}(\text{CO})_4(\eta^{2:2}\text{-NBD})$ ,  $\text{Cr}(\text{CO})_4(\eta^{2:2}\text{-NBD})$  and  $\text{W}(\text{CO})_4(\eta^{2:2}\text{-NBD})$  were prepared by thermal

reaction of 2,5-norbornadiene (NBD) with  $M(\text{CO})_6$  (M= Cr, Mo, W) according to Scheme 2. Complexes (1a to 3e) were prepared by photochemical reaction as shown in Scheme 3. Analytical data for  $\{M(\text{CO})_4(\text{met-DTTT})_2\}$  (1a to 3a);  $\{M(\text{CO})_4(\text{eth-DTTT})_2\}$  (1b to 3b);  $\{M(\text{CO})_4(\text{n-pr-DTTT})_2\}$  (1c to 3c);  $\{M(\text{CO})_4(\text{ph-DTTT})_2\}$  (1d to 3d) and  $\{M(\text{CO})_4(\text{benz-DTTT})_2\}$  (1e to 3e); where M= Cr, Mo and W; complexes are given in Table 1. The photogeneration of  $M(\text{CO})_5$  from  $M(\text{CO})_6$  (M=Cr, Mo and W) has been extensively studied. These 16-electron  $M(\text{CO})_5$  fragments react quickly with any available donor atom to yield a  $M(\text{CO})_5\text{L}$  species; and where L is a chelating bidentate ligand, rapid continuation to the chelating  $M(\text{CO})_4\text{L}$  or bridging  $M_2(\text{CO})_{10}$  ( $\mu\text{-L}$ ) products may occur (Cotton and Wilkinson, 1988; Sema et al., 2003; Ozan et al., 2003; Almond et al., 1997). The photochemical reactions of  $\text{Mo}(\text{CO})_4(\eta^{2:2}\text{-NBD})$  with DTTT proceed in an entirely expected manner by displacement of the NBD ligand to give the monometallic complexes (1a to 3e).

**Table 1.** Physical and analytical data of Complexes  $\{M(CO)_4(L)_2\}$  (L = met-DTTT, eth-DTTT, n-pr-DTTT, ph-DTTT and benz-DTTT) (M = Cr, Mo, W).

Complexes	Empirical formula	Yield %	Found (calculated), %				Mol. wt
			C	H	N	S	
1a	C <sub>14</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> Cr	75	33.12 (34.42)	4.02 (4.13)	11.16 (11.47)	25.28 (26.25)	484 (489)
2a	C <sub>14</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> Mo	71	30.86 (31.58)	3.57 (3.79)	10.37 (10.52)	23.67 (24.08)	529 (533)
3a	C <sub>14</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> W	67	26.25 (27.10)	3.07 (3.25)	8.32 (9.03)	19.28 (20.67)	615 (620)
1b	C <sub>18</sub> H <sub>28</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> Cr	73	38.76 (39.69)	5.01 (5.18)	9.98 (10.29)	23.08 (23.55)	541 (545)
2b	C <sub>18</sub> H <sub>28</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> Mo	74	35.12 (36.73)	4.12 (4.79)	9.05 (9.52)	21.12 (21.79)	585 (589)
3b	C <sub>18</sub> H <sub>28</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> W	68	30.98 (31.96)	4.01 (4.17)	8.00 (8.28)	18.29 (18.96)	673 (677)
1c	C <sub>22</sub> H <sub>36</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> Cr	72	43.07 (43.98)	5.76 (6.04)	8.95 (9.33)	20.56 (21.35)	596 (601)
2c	C <sub>22</sub> H <sub>36</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> Mo	73	39.94 (40.98)	5.03 (5.63)	8.04 (8.69)	18.44 (19.89)	641 (645)
3c	C <sub>22</sub> H <sub>36</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> W	69	35.47 (36.07)	4.54 (4.95)	7.13 (7.65)	16.94 (17.51)	727 (733)
1d	C <sub>34</sub> H <sub>28</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> Cr	70	54.57 (55.42)	3.27 (3.83)	7.13 (7.60)	16.89 (17.41)	733 (737)
2d	C <sub>34</sub> H <sub>28</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> Mo	72	51.65 (52.30)	3.22 (3.61)	6.97 (7.18)	16.01 (16.43)	777 (781)
3d	C <sub>34</sub> H <sub>28</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> W	66	46.12 (47.01)	3.00 (3.25)	6.02 (6.45)	14.02 (14.76)	863 (869)
1e	C <sub>38</sub> H <sub>36</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> Cr	76	56.86 (57.56)	4.04 (4.58)	6.54 (7.07)	15.78 (16.17)	787 (793)
2e	C <sub>38</sub> H <sub>36</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> Cr	74	53.76 (54.54)	3.94 (4.34)	6.09 (6.69)	14.79 (15.32)	832 (837)
3e	C <sub>38</sub> H <sub>36</sub> O <sub>4</sub> N <sub>4</sub> S <sub>4</sub> Cr	70	48.76 (49.35)	3.76 (3.92)	5.87 (6.06)	13.22 (13.87)	921 (925)

**Table 2a.** Selected IR bands (cm<sup>-1</sup>) and <sup>1</sup>H-NMR (ppm) data of ligands.

Ligand	Name of ligands	Abbreviation	(C-S-C)	$\nu_{as(C=S)}$	<sup>1</sup> H-NMR (in CDCl <sub>3</sub> ) $\delta$ ppm
a	3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione	met-DTTT	837	628	2.46 (s, 3H, 5-CH <sub>3</sub> ), 3.30 (s, 3H, 3-CH <sub>3</sub> ), 1.27 (s, 2H, 2-CH <sub>2</sub> ), 4.34 (s, 2H, 4-CH <sub>2</sub> )
b	3,5-diethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione	eth-DTTT	837	632	0.90 (t, 3H, 5-CH <sub>2</sub> CH <sub>3</sub> ), 2.38 (q, 2H, 5-CH <sub>2</sub> CH <sub>3</sub> ), 1.72 (t, 3H, 3-CH <sub>2</sub> CH <sub>3</sub> ), 3.18 (q, 2H, 3-CH <sub>2</sub> CH <sub>3</sub> ), 1.27 (s, 2H, 2-CH <sub>2</sub> ), 4.34 (s, 2H, 4-CH <sub>2</sub> )
c	3,5-di-n-propyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione	n-pr-DTTT	836	637	1.04 (t, 3H, 5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 2.07 (m, 2H, 5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 4.37 (t, 2H, 5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 1.84 (t, 3H, 3-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 2.87 (m, 2H, 3-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 5.16 (t, 2H, 3-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 1.26 (s, 2H, 2-CH <sub>2</sub> ), 4.33 (s, 2H, 4-CH <sub>2</sub> )
d	3,5-diphenyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione	ph-DTTT	835	635	7.46 (m, 5H, 5-C <sub>6</sub> H <sub>5</sub> ), 7.90 (m, 5H, 3-C <sub>6</sub> H <sub>5</sub> ), 1.26 (s, 2H, 2-CH <sub>2</sub> ), 4.34 (s, 2H, 4-CH <sub>2</sub> )
e	3,5-dibenzyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione	benz-DTTT	836	639	7.46 (m, 5H, 5-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 4.32 (m, 2H, 5-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 7.96 (m, 5H, 3-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 5.12 (m, 2H, 3-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 1.27 (s, 2H, 2-CH <sub>2</sub> ), 4.34 (s, 2H, 4-CH <sub>2</sub> )

The IR Spectral bands and <sup>1</sup>H-NMR data of ligands (L = met-DTTT (a); eth-DTTT (b); n-pr-DTTT (c); ph-DTTT (d); benz-DTTT (e) ) are presented in Table 2a. In this study, photochemical reactions of M(CO)<sub>4</sub>(NBD) (M=Cr, Mo and W) with met-DTTT (a); eth-DTTT (b); n-pr-DTTT (c); ph-DTTT (d) and benz-DTTT (e) ligands occurs in this expected manner, and gave hither to a series of complexes (1a) to (1e); (2a) to (2e) and (3a) to (3e) occur via the displacement of NBD from M(CO)<sub>4</sub>(NBD) (M=Cr, Mo and W) and co-ordination of metal atom via two Sulfur

donor atoms (C=S) of two molecules of the ligand yielding cis-M(CO)<sub>4</sub>L<sub>2</sub> complexes. Important IR spectral bands M(CO)<sub>4</sub>L<sub>2</sub> (L = met-DTTT (a); eth-DTTT (b); n-pr-DTTT (c); ph-DTTT (d); benz-DTTT (e) and M=Cr, Mo and W) are presented in Table 2b.

The evidence about the metal-sulfur (M-S) bond formation is the appearance of a new band in all the complexes around 385 to 403 cm<sup>-1</sup>, which may be assigned to the  $\nu(M-S)$  mode (Hiral et al., 2008, Amin et al., 2001; Jian et al., 1999) can be correlated with the

**Table 2b.** Selected IR bands ( $\text{cm}^{-1}$ ) and ( $^1\text{H}$ )-NMR (ppm) data of  $\{\text{M}(\text{CO})_4(\text{L})_2\}$  (L= (a): met-DTTT, R=CH<sub>3</sub>; (b): eth-DTTT, R=C<sub>2</sub>H<sub>5</sub>; (c): n-Pr-DTTT, R=C<sub>3</sub>H<sub>7</sub>; (d): ph-DTTT, R=C<sub>6</sub>H<sub>5</sub> and (e): benz-DTTT, R= C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) (M = (1): Cr, (2): Mo, (3): W).

Complexes	$\nu(\text{CO}) \text{ cm}^{-1}$	(C-S-C)	$\nu_{\text{sym}}$ (C=S)	$\nu_{\text{as}}$ (C=S)	$^1\text{H-NMR}$ (in $\text{CDCl}_3$ ) $\delta$ ppm
1a	2015, 1943, 1910, 1850	836	668	610	2.44 (s, 3H, 5-CH <sub>3</sub> ), 3.27 (s, 3H, 3-CH <sub>3</sub> ), 1.26 (s, 2H, 2-CH <sub>2</sub> ), 4.33 (s, 2H, 4-CH <sub>2</sub> )
2a	2010, 1912, 1845, 1795	835	664	607	2.45 (s, 3H, 5-CH <sub>3</sub> ), 3.28 (s, 3H, 3-CH <sub>3</sub> ), 1.25 (s, 2H, 2-CH <sub>2</sub> ), 4.32 (s, 2H, 4-CH <sub>2</sub> )
3a	2005, 1851, 1832, 1782	838	666	608	2.44 (s, 3H, 5-CH <sub>3</sub> ), 3.29 (s, 3H, 3-CH <sub>3</sub> ), 1.26 (s, 2H, 2-CH <sub>2</sub> ), 4.33 (s, 2H, 4-CH <sub>2</sub> )
1b	2012, 1938, 1904, 1848	838	670	612	0.89 (t, 3H, 5-CH <sub>2</sub> CH <sub>3</sub> ), 2.32 (q, 2H, 5-CH <sub>2</sub> CH <sub>3</sub> ), 1.71 (t, 3H, 3-CH <sub>2</sub> CH <sub>3</sub> ), 3.16 (q, 2H, 3-CH <sub>2</sub> CH <sub>3</sub> ), 1.26 (s, 2H, 2-CH <sub>2</sub> ), 4.32 (s, 2H, 4-CH <sub>2</sub> )
2b	2007, 1908, 1842, 1790	836	667	610	0.88 (t, 3H, 5-CH <sub>2</sub> CH <sub>3</sub> ), 2.34 (q, 2H, 5-CH <sub>2</sub> CH <sub>3</sub> ), 1.70 (t, 3H, 3-CH <sub>2</sub> CH <sub>3</sub> ), 3.17 (q, 2H, 3-CH <sub>2</sub> CH <sub>3</sub> ), 1.25 (s, 2H, 2-CH <sub>2</sub> ), 4.32 (s, 2H, 4-CH <sub>2</sub> )
3b	2006, 1854, 1835, 1787	835	664	611	0.89 (t, 3H, 5-CH <sub>2</sub> CH <sub>3</sub> ), 2.33 (q, 2H, 5-CH <sub>2</sub> CH <sub>3</sub> ), 1.72 (t, 3H, 3-CH <sub>2</sub> CH <sub>3</sub> ), 3.17 (q, 2H, 3-CH <sub>2</sub> CH <sub>3</sub> ), 1.26 (s, 2H, 2-CH <sub>2</sub> ), 4.33 (s, 2H, 4-CH <sub>2</sub> )
1c	2014, 1942, 1907, 1850	837	665	615	1.02 (t, 3H, 5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 2.06 (h, 2H, 5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 4.32 (t, 2H, 5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 1.82 (t, 3H, 3-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 2.84 (h, 2H, 3-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 5.10 (t, 2H, 3-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 1.25 (s, 2H, 2-CH <sub>2</sub> ), 4.32 (s, 2H, 4-CH <sub>2</sub> )
2c	2006, 1910, 1841, 1792	835	663	618	1.01 (t, 3H, 5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 2.05 (h, 2H, 5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 4.34 (t, 2H, 5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 1.81 (t, 3H, 3-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 2.83 (h, 2H, 3-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 5.12 (t, 2H, 3-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 1.24 (s, 2H, 2-CH <sub>2</sub> ), 4.31 (s, 2H, 4-CH <sub>2</sub> )
3c	2002, 1856, 1832, 1788	836	662	617	1.03 (t, 3H, 5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 2.06 (h, 2H, 5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 4.35 (t, 2H, 5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 1.82 (t, 3H, 3-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 2.84 (h, 2H, 3-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 5.11 (t, 2H, 3-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 1.25 (s, 2H, 2-CH <sub>2</sub> ), 4.33 (s, 2H, 4-CH <sub>2</sub> )
1d	2017, 1948, 1908, 1853	836	672	614	7.42 (m, 5H, 5-C <sub>6</sub> H <sub>5</sub> ), 7.87 (m, 5H, 3-C <sub>6</sub> H <sub>5</sub> ), 1.25 (s, 2H, 2-CH <sub>2</sub> ), 4.33 (s, 2H, 4-CH <sub>2</sub> )
2d	2008, 1906, 1844, 1794	837	669	613	7.43 (m, 5H, 5-C <sub>6</sub> H <sub>5</sub> ), 7.88 (m, 5H, 3-C <sub>6</sub> H <sub>5</sub> ), 1.24 (s, 2H, 2-CH <sub>2</sub> ), 4.31 (s, 2H, 4-CH <sub>2</sub> )
3d	2010, 1860, 1831, 1790	838	664	616	7.44 (m, 5H, 5-C <sub>6</sub> H <sub>5</sub> ), 7.89 (m, 5H, 3-C <sub>6</sub> H <sub>5</sub> ), 1.26 (s, 2H, 2-CH <sub>2</sub> ), 4.33 (s, 2H, 4-CH <sub>2</sub> )
1e	2020, 1943, 1902, 1852	837	672	616	7.42 (m, 5H, 5-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 4.31 (m, 2H, 5-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 7.91 (m, 5H, 3-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 5.10 (m, 2H, 3-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 1.26 (s, 2H, 2-CH <sub>2</sub> ), 4.34 (s, 2H, 4-CH <sub>2</sub> )
2e	2011, 1910, 1846, 1802	835	669	622	7.43 (m, 5H, 5-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 4.32 (m, 2H, 5-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 7.92 (m, 5H, 3-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 5.11 (m, 2H, 3-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 1.27 (s, 2H, 2-CH <sub>2</sub> ), 4.33 (s, 2H, 4-CH <sub>2</sub> )
3e	2014, 1863, 1834, 1791	836	665	619	7.44 (m, 5H, 5-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 4.32 (m, 2H, 5-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 7.96 (m, 5H, 3-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 5.10 (m, 2H, 3-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 1.26 (s, 2H, 2-CH <sub>2</sub> ), 4.33 (s, 2H, 4-CH <sub>2</sub> )

decrease in  $\nu(\text{CO})$  modes of (1a to 3e) complexes move to lower wave numbers in comparison with the starting  $\text{M}(\text{CO})_6$  ( $\text{M}=\text{Cr}$ ,  $\text{Mo}$  and  $\text{W}$ ) molecules (Cotton and Wilkinson, 1988; Mahmud et al., 2007; Maurya et al., 1992). This decrease in the frequency of CO absorption is because of the accumulation of charge density on metal atom ( $\text{Cr}$ ,  $\text{Mo}$  and  $\text{W}$ ) which stabilizes itself by transferring it back to the nearby CO (a  $\pi$ -acceptor ligand) (Ayodhya, 1999).

Four bands in the range of 2002 to 2020  $\text{cm}^{-1}$ , 1851 to 1948  $\text{cm}^{-1}$ , 1831 to 1910  $\text{cm}^{-1}$  and 1782 to 1853  $\text{cm}^{-1}$ , arising from  $\nu(\text{CO})$  vibrations, are seen which presumably have local  $c_{2v}$  symmetry of  $\text{M}(\text{CO})_4$  unit in  $\{\text{M}(\text{CO})_4(\text{met-DTTT})_2\}$  (1a to 3a),  $\{\text{M}(\text{CO})_4(\text{eth-DTTT})_2\}$  (1b to 3b),  $\{\text{M}(\text{CO})_4(\text{n-pr-DTTT})_2\}$  (1c to 3c),  $\{\text{M}(\text{CO})_4(\text{ph-DTTT})_2\}$  (1d to 3d) and  $\{\text{M}(\text{CO})_4(\text{benz-DTTT})_2\}$  (1e to 3e); where  $\text{M} = \text{Cr}$ ,  $\text{Mo}$  and  $\text{W}$  complexes (Scheme 3). These values are in close resemblance to the values of  $\nu(\text{CO})$  vibration for other sulfur containing di-substituted group-6 metal carbonyls (Cotton and Kraihanzel, 1962; Ozer and Ozkar, 1999; Ayodhya et al., 2010; Timmers and Wacholtz, 1994). The presence of normal ligand bands indicated that these bands were intact in the complexes. The nature and number of CO bands resemble closely to the bands of other known di- and tri-substituted metal carbonyls (Ayodhya et al., 2010; Sema et al., 2003; Darensbourg and Darensbourg, 1970, Abel et al., 1958).

The IR spectra data for (1a to 3e) show a decrease in  $\nu(\text{C}=\text{S})$  on coordination. In the free ligand, the IR active mode  $\nu(\text{C}=\text{S})$  is at 628  $\text{cm}^{-1}$  for met-DTTT (Cotton and Kraihanzel, 1962). On coordination, two bands are observed in the range of 666 to 668  $\text{cm}^{-1}$  [ $\nu_{\text{sym}}(\text{C}=\text{S})$ ] and 607 to 610  $\text{cm}^{-1}$  [ $\nu_{\text{as}}(\text{C}=\text{S})$ ]; 660 to 670  $\text{cm}^{-1}$  [ $\nu_{\text{sym}}(\text{C}=\text{S})$ ] and 610 to 612  $\text{cm}^{-1}$  [ $\nu_{\text{as}}(\text{C}=\text{S})$ ]; 662 to 665  $\text{cm}^{-1}$  [ $\nu_{\text{sym}}(\text{C}=\text{S})$ ] and 615 to 618  $\text{cm}^{-1}$  [ $\nu_{\text{as}}(\text{C}=\text{S})$ ]; 664 to 672  $\text{cm}^{-1}$  [ $\nu_{\text{sym}}(\text{C}=\text{S})$ ] and 613 to 616  $\text{cm}^{-1}$  [ $\nu_{\text{as}}(\text{C}=\text{S})$ ]; and 665 to 672  $\text{cm}^{-1}$  [ $\nu_{\text{sym}}(\text{C}=\text{S})$ ] and 616 to 622  $\text{cm}^{-1}$  [ $\nu_{\text{as}}(\text{C}=\text{S})$ ] in the case of met-DTTT, eth-DTTT, n-pr-DTTT, ph-DTTT and benz-DTTT respectively. As expected four bands arising from  $\nu(\text{CO})$  vibrations are seen for each complex which presumably have local  $C_{2v}$  symmetry of the  $\text{M}(\text{CO})_4$  unit (Sema et al, 2003) and confirming the cis- complexes (Darensbourg and Darensbourg, 1970).

In addition, magnetic susceptibility measurement shows that (1a to 3e) complexes were diamagnetic. Since these complexes have  $\text{M}(0)$  [ $\text{M}=\text{Cr}$ ,  $\text{Mo}$ ,  $\text{W}$ ] with a low spin  $d_6$  configuration. Such diamagnetism might arise from further splitting of the d-orbital in the low symmetry complexes, that is,  $d_{xy}^2$ ,  $d_{xz}^2$ ,  $d_{yz}^2$ ,  $d_{(x^2-y^2)}^2$ , and  $d_{z^2}$  (Senem et al., 2008, Ayodhya et al., 2010).

## Conclusion

The IR spectroscopic results show that the ligands (a to e) coordinate via sulfur ( $\text{C}=\text{S}$ ) atom in (1a to 3e) and these ligands behave as monodentate ligand. The IR

data are well in accord with cis- coordination of ligands. These results suggest that the ligands

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