Synthesis and Characterization of Group-6 Metal Carbonyl Complexes of Aroyl Hydrazone Derivatives

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Abstract: Carbonyl complexes of Chromium, molybdenum and tungsten of composition, $[M(CO)_4L-L]$, (where $M = Cr, Mo$ or W and $L-L =$ benzoic acid[1-(Furan-2-yl)methylene]hydrazide (BFMH), benzoic acid[(thiophene-2-yl)methylene]hydrazide (BTMH), benzoic acid[1-(thiophene-2-yl)ethylidene]hydrazide (BTEH), benzoic acid (phenylmethylene)hydrazide (BPMH) and benzoic acid[1-(anisol-3-yl)methylene] hydrazide (BAMH) are reported. These have been prepared by refluxing metal carbonyls and the ligands in 1:1molar ratio. The complexes were characterized by elemental analysis, IR spectra, UV-vis spectra, 1H NMR, TGA/DTA, conductivity and magnetic susceptibility measurements. The IR bands suggest that in all the complexes the ligands behave as neutral bidentate chelating type coordinating metal through carbonyl oxygen and azomethine nitrogen. The CO force constants and CO-CO interaction constants for these derivatives have been calculated using Cotton-Kraihanzel secular equations, which indicate poor π -bonding ability of the coordinated ligands.

Keywords: Carbonyl complexes, Cotton-Kraihanzel secular equations, Bidentate ligands, Molybdenum, Tungsten, Schiff bases.

Introduction

The chemistry of metal carbonyls has been of considerable interest for several decades mainly due to structural aspects and reactivity of these compounds in respect to several classes of organic ligands, and also by their applications in catalysis and in electronic devices based on non-linear optical effects¹⁻⁴. Transition metal carbonyl derivatives are intermediates in homogeneous catalytic reactions such as carbonylation, hydrogenation, hydroformylation and oxygen transfer⁵. They are common starting materials for the synthesis of other low- valent metal complexes, especially clusters. The carbonyl ligands can not only be substituted by a large number of other ligands (lewis bases, olefins, and arenes), but the remaining carbonyl groups stabilize the molecules against oxidation or thermal decomposition. Carbonyl groups are also useful probe for determining the electronic and

molecular structure of organometallic species by spectroscopic methods⁶. Research on preparation, structures and applications of metal carbonyls and their derivatives has been intense for several decades. The first metal carbonyl, Ni(CO)₄, was prepared by A. Mond and co-workers⁷ in 1890 by the reaction of metallic nickel with carbon monoxide. It found application immediately and has been used for industrial preparation of pure nickel. Many other carbonyls were synthesized shortly thereafter⁸. Carbonyl complexes of group 6 which contain nitrogen and phosphorus ligands exhibit an interesting and varied chemistry⁹⁻¹¹. Reports on 2, 2' – bipyridine (bipy) substituted tetracarbonyls and tricarbonyl phosphine complexes and their structural investigation emerged from literature many years ago¹². S, N-ligated derivatives of hexacarbonyltungsten(0), [NEt₄] [W(CO)₄L-L] (L-L = 2-thiouracilate and 6-methyl-2-thiouracilate) have been synthesized from reaction of photogenerated W(CO)₅(solvent) (solvent = MeOH or THF) and corresponding [Et₄N] [thiouracilate]¹³. Novel orotic acid derivatives of tungsten carbonyl, [Et₄N]₂[W(CO)₄(orotate)], [Et₄N]₂[W(CO)₄(dihydroorotate)] [where orotate = (C₅H₂O₄N₂)²⁻, dihydroorotate = (C₅H₄O₄N₂)²⁻] have been reported and found to be O,N-ligated complexes^{14,15}. Chromium, manganese, cobalt, nickel and ruthenium carbonyl complexes with a wide variety of ligands having donor atom sets such as N₂O₂, NO₂ and N₄ around the metal ion have been used as catalysts for epoxidation reactions¹⁶⁻¹⁹. In the present study we have used ligands namely benzoic acid[1-(Furan-2-yl)methylene]hydrazide (BFMH), benzoic acid[(thiophene-2-yl)methylene]hydrazide (BTMH), benzoic acid[1-(thiophene-2-yl)ethylidene]hydrazide (BTEH), benzoic acid (phenylmethylene)hydrazide (BPMH) and benzoic acid[1-(anisole-3-yl)methylene] hydrazide (BAMH) in the CO displacement reactions of M(CO)₆ (where M = Cr, Mo and W), yielding *cis*-disubstituted products, [M(CO)₄L-L] (where L-L = aroylhydrazone ligands). The structures of ligands are given below:

BFMH where X = O & R = H
 BTMH where X = S & R = H
 BTEH where X = S & R = CH₃

BPMH Where R¹ = H
 BAMH where R¹ = OCH₃

Experimental

Reagent grade furfuraldehyde (Himedia), thiophen-2-carboxaldehyde (Himedia), 2-acetylthiophene (Himedia), benzaldehyde (Ranbaxy), anisaldehyde (Himedia), benzhydrazide (Fluka), THF (Ranbaxy), chromium hexacarbonyl (Aldrich), molybdenum hexacarbonyl (Aldrich), and tungsten hexacarbonyl (Aldrich) were used as received. The solvent used for the synthesis of ligands and their complexes were distilled before use. The ligands were prepared by the reported method²⁰.

Methods and instruments

Carbon, hydrogen, nitrogen and sulphur were analysed microanalytically using CHNS analyzer Leco make model-932. Metals analysis was done by gravimetric method²¹. Molar conductivity at room temperature in DMF (10^{-3}M) was measured using an Elico conductivity Bridge, type CM82T and a conductivity cell with cell constant of 0.74. Magnetic susceptibility of the complexes was recorded at room temperature using Gouy's balance and using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a standard. IR spectra of complexes over the region $4000\text{--}400\text{ cm}^{-1}$ were recorded on a Perkin Elmer FTIR spectrophotometer using KBr disc. The electronic spectra of the complexes were recorded using a double beam UV–visible spectrophotometer type SL-164. Thermogravimetric analysis (DTA-DTG-TG) of complexes was recorded on Perkin Elmer (Pyris Diamond) thermoanalyser at the heating rate of $10^\circ\text{C}/\text{min}$ in the atmosphere of air.

Preparation of complexes

[Cr(CO)₄L-L]

$\text{Cr}(\text{CO})_6$ (0.659 g, 3 mmol) and the ligand (3 mmol): benzoic acid[1-(Furan-2-yl)methylene]hydrazide (BFMH) (0.642 g), benzoic acid [(thiophene-2-yl)methylene]hydrazide (BTMH) (0.690 g), benzoic acid [1-(thiophene-2-yl) ethylidene] hydrazide (BTEH) (0.732 g), benzoic acid (phenylmethylene) hydrazide (BPMH) (0.672 g) and benzoic acid [1-(anisol-3-yl) methylene] hydrazide (BAMH) (0.762 g)] were refluxed in 50 ml of THF for about 7–8 h under dry conditions in an atmosphere of nitrogen. The yellow solution obtained in each case was allowed to cool and coloured, air stable solid was obtained by evaporating the solvent in vacuo. Unreacted materials were removed by washing the residue several times with n-hexane. The product was recrystallized in THF (Yield: 60–65%). The reaction was repeated with 1:2, 1:3 molar ratios of hexacarbonyl chromium(0) and corresponding ligand and same product was isolated in each case.

[Mo(CO)₄L-L]

$\text{Mo}(\text{CO})_6$ (264 mg, 1.0 mmol) and the ligand (1.0 mmol): benzoic acid[1-(Furan-2-yl)methylene] hydrazide (BFMH) (0.214 g), benzoic acid [(thiophene-2-yl)methylene] hydrazide (BTMH) (0.230 g), benzoic acid [1-(thiophene-2-yl)ethylidene] hydrazide (BTEH) (0.244 g), benzoic acid (phenylmethylene) hydrazide (BPMH) (0.224 g) and benzoic acid[1-(anisol-3-yl)methylene] hydrazide (BAMH) (0.254 g)] were dissolved in xylene (30 ml). The solution was refluxed for 4–5 hours. After cooling to room temperature, the solvent was removed in vacuo and the residue was dissolved in chloroform: dichloromethane (5:2) and left to stand for two days for crystallization at room temperature. The solvent was decanted and the crystals were dried in vacuo (Yield: 70–80%). The reaction was repeated with 1:2, 1:3 molar ratios of hexacarbonyl molybdenum(0) and corresponding ligand and same product was isolated in each case.

[W(CO)₄L-L]

$\text{W}(\text{CO})_6$ (1.05 g, 3 mmol) and the ligand (3 mmol): benzoic acid[1-(Furan-2-yl)methylene] hydrazide (BFMH) (0.642 g), benzoic acid[(thiophene-2-yl)methylene] hydrazide (BTMH) (0.690 g), benzoic acid[1-(thiophene-2-yl)ethylidene]hydrazide (BTEH) (0.732 g), benzoic acid (phenylmethylene)hydrazide (BPMH) (0.672 g) and benzoic acid[1-(anisol-3-yl)methylene]hydrazide (BAMH) (0.762 g)] were refluxed in 50 ml of THF for about 7–8 h under dry conditions in an atmosphere of nitrogen. The yellow solution obtained in each case was allowed to cool and the yellow orange, air stable solid was obtained by evaporating the solvent in vacuo. Unreacted materials were removed by washing the residue several times with n-hexane. The product was recrystallized in THF (Yield: 70–80%). The reaction

was repeated with 1:2, 1:3 molar ratios of hexacarbonyl tungsten(0) and corresponding ligand and same product was isolated in each case.

Results and Discussion

The analytical and physical data (Table 1) showed that all complexes are mononuclear with general formula, $[M(CO)_4L-L]$ (where L-L = benzoic acid [1-(Furan-2-yl) methylene] hydrazide (BFMH), benzoic acid [(thiophene-2-yl) methylene] hydrazide (BTMH), benzoic acid [1-(thiophene-2-yl)ethylidene] hydrazide (BTEH), benzoic acid (phenylmethylene) hydrazide (BPMH) and benzoic acid[1-(anisol-3-yl) methylene] hydrazide (BAMH) and M = Cr, Mo, and W). All the complexes are coloured, stable in air and soluble in THF, DMSO and DMF. The complexes have characteristic melting points. Moreover, magnetic susceptibility measurement at 30 °C indicates the diamagnetic nature of complexes.

Table 1. Analytical data and some physical properties of the synthesized complexes $cis-[M(CO)_4(L-L)]$.

$\sum \chi_i$	Complex	Mol. wt. g/mol	Colour	M.P., °C	Found (Calculated)					Molar conductivity mho cm ² mol ⁻¹
					C	H	N	S	M	
1	Cr(CO) ₄ BFMH	434.21	Bright Yellow	110	44.11 (44.27)	2.11 (2.30)	7.00 (6.44)		11.48 (11.97)	21
2	Cr(CO) ₄ BTMH	450.21	Dark Brown	105	43.11 (42.70)	2.44 (2.22)	6.30 (6.21)	7.14 (7.12)	11.44 (11.54)	28
3	Cr(CO) ₄ BTEH	464.30	Brown	123	44.12 (43.97)	3.12 (2.79)	6.10 (6.03)	6.95 (6.90)	11.89 (11.19)	18
4	Cr(CO) ₄ BPMH	442.24	Light Brown	128	49.23 (48.88)	2.92 (2.71)	6.41 (6.33)		12.23 (11.75)	28
5	Cr(CO) ₄ BAMH	472.27	Light Brown	130	48.82 (48.31)	3.26 (3.16)	6.00 (5.92)		11.51 (11.00)	30
6	Mo(CO) ₄ BFMH	422.16	Black	230	45.12 (45.54)	3.00 (2.36)	6.87 (6.63)		21.89 (22.72)	15
7	Mo(CO) ₄ BTMH	438.22	Dark Brown	240	44.12 (43.86)	2.36 (2.28)	6.39 (6.38)	7.50 (7.31)	21.13 (21.89)	18
8	Mo(CO) ₄ BTEH	452.25	Dark Brown	245	45.12 (45.14)	3.25 (3.05)	6.22 (6.19)	7.12 (7.07)	21.10 (21.21)	34
9	Mo(CO) ₄ BPMH	432.19	Black	246	50.87 (50.01)	2.82 (2.77)	6.60 (6.47)		21.63 (22.19)	29
10	Mo(CO) ₄ BAMH	462.22	Black	253	50.11 (49.36)	3.30 (3.24)	5.25 (5.19)		20.12 (20.75)	29
11	W(CO) ₄ BFMH	509.92	Yellow	149	37.58 (37.70)	2.01 (1.96)	6.00 (5.94)		35.99 (36.08)	20
12	W(CO) ₄ BTMH	526.02	Bright Yellow	140	36.99 (36.54)	2.01 (1.90)	5.57 (5.34)	6.10 (6.09)	33.95 (34.94)	28
13	W(CO) ₄ BTEH	539.05	Yellow	152	37.89 (37.87)	2.24 (2.41)	5.37 (5.19)	6.01 (5.94)	33.12 (34.10)	22
14	W(CO) ₄ B PMH	519.99	Light yellow	158	41.82 (41.57)	2.66 (2.30)	5.18 (5.38)		35.01 (35.35)	15
15	W(CO) ₄ B AMH	550.02	Light Yellow	160	42.01 (41.48)	2.87 (2.72)	5.11 (5.09)		33.14 (33.42)	21

Conductance measurement

The molar conductivity (measured in 10^{-3} M DMF solution) of these complexes is in the range of 15-34 mho $\text{cm}^2 \text{mol}^{-1}$ which is much less than the value of 70-160 mho $\text{cm}^2 \text{mol}^{-1}$ for 1:1 electrolyte in this solvent. Thus, these complexes are undissociated which indicates the non-electrolytic nature of these complexes.

Infrared spectra

The CO force constants and CO-CO interaction constants for these derivatives have been calculated using Cotton-Kraihanzel secular equations²².

$$2A1 \begin{vmatrix} \mu(k_2 + 2k_i) - 2\mu k_i & \\ 2\mu k_i & \mu(k_1 + k_i) - \lambda \end{vmatrix} = 0 \quad (1)$$

$$B_1 \lambda = \mu(k_2 - 2k_i) \quad (2)$$

$$B_2 \lambda = \mu(k_1 - k_i) \quad (3)$$

In these equations, k_1 = stretching force constant for CO groups trans to ligands, k_2 = stretching force constant for CO groups cis to ligands, k_i = CO-CO interaction force constant, μ = reciprocal of reduced mass of CO (0.14583) and $A = (5.8890 \times 10^{-2} \nu^2)$ where ν = frequency in cm^{-1} and the force constants are in dynes cm^{-1} .

All the complexes show four CO stretching bands in the infra red region 2075-1825 cm^{-1} due to $2A_1 + B_1 + B_2$ modes as expected for C_{2v} symmetry and in agreement with their *cis*-configuration.²²⁻²⁵ The frequencies for the complexes of unsymmetrical ligands are assigned as follows. The higher frequency A_1 and B_1 bands are assigned to *trans*-carbonyl ligands, while the lower frequency A_1 and B_2 bands are assigned to *cis*-carbonyl ligands.

The values of k_1 , k_2 and k_i for tungsten complexes were found in the ranges 14.09-14.44, 15.87-16.08 and 0.23-0.25 mdynes/A^0 respectively, the values of k_1 , k_2 and k_i for molybdenum complexes were found in the ranges 13.75-13.96, 15.69-16.03 and 0.26-0.32 mdynes/A^0 respectively and the values of k_1 , k_2 and k_i for chromium complexes were found in the ranges 13.81-14.00, 15.59-15.80 and 0.20-0.25 mdynes/A^0 respectively, which confirm the validity of vibrational mode assignments. The values of CO stretching force constants in the complexes are lower than that for W(CO)_6 (16.41 mdynes/A^0), Mo(CO)_6 (16.52 mdynes/A^0) and Cr(CO)_6 (16.49 mdynes/A^0) indicating the replacement of two CO groups by the ligand (L-L) and poor pi-bonding ability of the ligands used^{26,27}. These values are close to the values of force constants deduced for other nitrogen containing *cis*-disubstituted group 6 metal carbonyls^{28,29}.

Moreover, the IR bands appearing in the spectra of the free ligands (aroylhydrazone) at ca. 1660 and 1640 cm^{-1} are attributed to amide $\nu(\text{C=O})$ and $\nu(\text{C=N})$ modes respectively³⁰. The spectra of free ligands exhibit $\nu(\text{N-H})$ stretching band at ca. 3250 and $\nu(\text{C=N})$ bands ca. 1640 cm^{-1} indicating that ligands exist in keto form. The presence of $\nu(\text{N-H})$ bands in the spectra of the complexes suggest that all the ligands remain protonated on complexation to metal. The amide bands $\nu(\text{C=O})$ and $\nu(\text{C=N})$ shift to lower frequencies (Table 2) in the spectra of complexes suggesting the involvement of carbonyl oxygen and azomethine nitrogen in coordination to metal³¹. Thus, these observations suggest that the ligands behave as neutral bidentate chelating type coordinating metal through carbonyl oxygen and azomethine nitrogen. The Ir spectra of two representative complexes namely $\text{Mo(CO)}_4\text{BFMH}$ and $\text{Mo(CO)}_4\text{BTMH}$ are given in Figure 1 and 2 respectively.

Table 2 IR spectral data(cm^{-1}) and CO force constants of $\text{cis-}[\text{M}(\text{CO})_4(\text{L-L})]$ Complexes.

S. No.	Complex	N (C=O)	N (C=N)	N (N-H)	$\nu(\text{C=O})$				Force constant ($\text{mdynes } \text{\AA}^{-1}$)		
					A_1	B_1	A_1	B_2 cis	k_1	K_2	K_3
1	$\text{Cr}(\text{CO})_4\text{BFMH}$	1627	1598	3242	2026	1947	19025	1835	13.81	15.75	0.22
2	$\text{Cr}(\text{CO})_4\text{BTMH}$	1627	1597	3244	2023	1940	1913	1845	14.00	15.59	0.25
3	$\text{Cr}(\text{CO})_4\text{BTEH}$	1631	1594	3258	2033	1939	1904	1835	13.84	15.68	0.25
4	$\text{Cr}(\text{CO})_4\text{BPMH}$	1628	1590	3255	2038	1947	1915	1844	13.98	15.80	0.20
5	$\text{Cr}(\text{CO})_4\text{BAMH}$	1629	1601	3273	2030	1941	1910	1845	13.99	15.69	0.24
6	$\text{Mo}(\text{CO})_4\text{BFMH}$	1631	1594	3242	2050	1955	1907	1853	13.85	15.95	0.26
7	$\text{Mo}(\text{CO})_4\text{BTMH}$	1631	1588	3258	2075	1950	1905	1840	13.96	15.93	0.29
8	$\text{Mo}(\text{CO})_4\text{BTEH}$	1631	1594	3258	2056	1932	1910	1825	13.76	15.69	0.32
9	$\text{Mo}(\text{CO})_4\text{BPMH}$	1628	1590	3256	2065	1957	1907	1834	13.84	16.03	0.28
10	$\text{Mo}(\text{CO})_4\text{BAMH}$	1622	1604	3273	2050	1943	1908	1826	13.75	15.82	0.26
11	$\text{W}(\text{CO})_4\text{BFMH}$	1648	1605	3322	2050	1964	1915	1859	14.21	16.08	0.25
12	$\text{W}(\text{CO})_4\text{BTMH}$	1648	1599	3258	2054	1958	1922	1872	14.38	15.93	0.23
13	$\text{W}(\text{CO})_4\text{BTEH}$	1640	1594	3258	2075	1962	1930	1875	14.44	16.04	0.25
14	$\text{W}(\text{CO})_4\text{BPMH}$	1634	1610	3235	2045	1952	1925	1859	14.19	15.87	0.24
15	$\text{W}(\text{CO})_4\text{BAMH}$	1642	1604	3260	2045	1964	1933	1852	14.09	16.05	0.24

Figure 1. IR spectrum of $[\text{Mo}(\text{CO})_4 \text{BFMH}]$.

Figure 2. IR spectrum of $[\text{Mo}(\text{CO})_4 \text{BTMH}]$.

Electronic spectra

Electronic spectra of mixed ligand carbonyl derivatives of the type $\text{cis-M}(\text{CO})_4 \text{L-L}$ ($\text{M}=\text{Cr}, \text{Mo}$ and W and L-L = a bidentate nitrogen ligand) have been extensively studied by Stufkens and collaborators^{32,33}.

The complexes under study exhibit three sharp spectral peaks (Table 3) in the region of 325-440 nm. These may be attributed to $\text{d} - \pi^* \text{CO}$ transitions. A peak of low intensity in the region of 475- 510 nm is also observed in these complexes which may be assigned to d-d transition.

Table 3. Electronic spectral data of $\text{cis-}[\text{M}(\text{CO})_4(\text{L-L})]$ Complexes.

S.No.	Complex	λ_{max} ($\text{d} - \pi^* \text{CO}$ Transition)	λ_{max} (d-d Transition)
1	$[\text{Cr}(\text{CO})_4 \text{BFMH}]$	325, 367, 393	498
2	$[\text{Cr}(\text{CO})_4 \text{BTMH}]$	349, 377, 403	478
3	$[\text{Cr}(\text{CO})_4 \text{BTEH}]$	336, 380, 393	510
4	$[\text{Cr}(\text{CO})_4 \text{BPMH}]$	345, 381, 392	501
5	$[\text{Cr}(\text{CO})_4 \text{BAMH}]$	352, 378, 405	499
6	$[\text{Mo}(\text{CO})_4 \text{BFMH}]$	328, 373, 399	484
7	$[\text{Mo}(\text{CO})_4 \text{BTMH}]$	325, 368, 440	510
8	$[\text{Mo}(\text{CO})_4 \text{BTEH}]$	339, 364, 413	476
9	$[\text{Mo}(\text{CO})_4 \text{BPMH}]$	338, 371, 418	490
10	$[\text{Mo}(\text{CO})_4 \text{BAMH}]$	348, 382, 419	497
11	$[\text{W}(\text{CO})_4 \text{BFMH}]$	346, 387, 329	479
12	$[\text{W}(\text{CO})_4 \text{BTMH}]$	357, 387, 418	497
13	$[\text{W}(\text{CO})_4 \text{BTEH}]$	353, 388, 412	478
14	$[\text{W}(\text{CO})_4 \text{BPMH}]$	362, 390, 422	493
15	$[\text{W}(\text{CO})_4 \text{BAMH}]$	332, 390, 408	475

^1H NMR

The ^1H NMR spectra of ligands in DMSO show low field signals at 11.8–11.4 ppm for the imino proton confirming the existence of ligands in keto form. The $\text{CH}=\text{N}$ peak is observed at 8.40–8.60 ppm and signal due to aromatic protons which occurs as multiplets appears between δ 6.4–7.8 ppm. The resonance signal due to CH_3 protons present in BTEH ligand occurs at 2.43 ppm. The spectra of all complexes show low field signals for imino proton at nearly same δ value as that of corresponding free ligands. Moreover, $\text{CH}=\text{N}$ peak in complexes is shifted towards higher delta value (8.78–9.12) due to deshielding because of bonding of azomethine nitrogen with metal. The ^1H NMR spectrum of a representative complex, $\text{W}(\text{CO})_4\text{BTMH}$ is given in Figure 3.

Figure 3. ^1H NMR spectrum of a representative complex $[\text{W}(\text{CO})_4\text{BTMH}]$.

TGA/DTA studies

The Thermogravimetric curves of the compounds were recorded in the temperature range of 25–800 $^{\circ}\text{C}$ in the atmosphere of air. The TGA curves of the representative complexes $[\text{W}(\text{CO})_4\text{BFMH}]$ and $[\text{Mo}(\text{CO})_4\text{BFMH}]$ indicate a continuous weight loss till a metal oxide is formed.

TGA/DTA of $[\text{W}(\text{CO})_4\text{BFMH}]$

The TG curve of the complex, $[\text{W}(\text{CO})_4\text{BFMH}]$ (Figure 4) shows a sharp weight loss starting from 100 $^{\circ}\text{C}$ upto 300 $^{\circ}\text{C}$ probably due to the loss of carbonyl groups. Thereafter a gradual but continuous weight loss takes place upto 600 $^{\circ}\text{C}$ probably due to the decomposition and loss of BFMH ligand. Further heating upto 800 $^{\circ}\text{C}$ does not show any weight loss indicating the formation of stable metal oxide, WO_2 (Calculated weight = 42.32% and observed weight = 42.42%). DTA curve also shows two exothermic peaks at 300 $^{\circ}\text{C}$ and 600 $^{\circ}\text{C}$ indicating decomposition of complex at 300 $^{\circ}\text{C}$ and 600 $^{\circ}\text{C}$ and oxidation of W to WO_2 and its crystallization.

Figure 4. TGA/DTA Studies of $[\text{W}(\text{CO})_4\text{BFMH}]$.

TGA/DTA of $[\text{Mo}(\text{CO})_4\text{BFMH}]$

The TG curve of the complex, $[\text{Mo}(\text{CO})_4\text{BFMH}]$ (Figure 5) shows a sharp weight loss starting from 200 °C up to 300 °C probably due to the loss of carbonyl groups. Thereafter a gradual but continuous weight loss takes place upto 600 °C probably due to the decomposition and loss of BFMH ligand. Further heating upto 800 °C donot show any weight loss indicating the formation of stable metal oxide, MoO_2 (Calculated weight = 30.30% and observed weight = 30.20%). DTA curve also shows two exothermic peaks at 300 °C and 600 °C indicating decomposition of complex at 300 °C and 600 °C and oxidation of Mo to MoO_2 and its crystallization.

Figure 5. TGA/DTA studies of $[\text{Mo}(\text{CO})_4\text{BFMH}]$.

Conclusion

Based on physicochemical and spectral studies, it is proposed that these complexes are mononuclear with composition, $[M(CO)_4L-L]$ having *cis* configuration, where L-L = benzoic acid[1-(Furan-2-yl)methylene]hydrazide (BFMH), benzoic acid[(thiophene-2-yl)methylene]hydrazide (BTMH), benzoic acid[1-(thiophene-2-yl)ethylidene]hydrazide (BTEH), benzoic acid (phenylmethylene) hydrazide (BPMH) and benzoic acid[1-(anisol-3-yl)methylene]hydrazide (BAMH) and M = Cr, Mo and W). IR spectral studies reveal that the ligands (L-L) behave as bidentate coordinating metal through carbonyl oxygen and azomethine nitrogen of the corresponding ligands. 1H NMR also reveals the coordination of ligand to metal through carbonyl oxygen and azomethine nitrogen. The electronic spectra of complexes show peaks responsible for d-d transition. Molar conductance of complexes indicates that these complexes behave as non-electrolytes and are undissociated in solutions. The Thermogravimetric curves of the compounds were recorded in the temperature range of 25-800 $^{\circ}C$ in the atmosphere of air. The TGA curves of the two representative complexes indicate a continuous weight loss till a metal oxide is formed. On the basis of above facts, following structure is proposed for these complexes.

M = Cr, Mo and W, L-L = BFMH, BTMH, BTEH, BPMH and BAMH

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