Synthesis and Characterization of Diarylthiourea Derivatives of Tungsten Carbonyl

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Reactions of five *sym*-diarylthioureas (L), *viz*,, *sym*-diphenylthiourea (dptu), *sym*-di-*o*-tolylthiourea (dottu), *sym*-di-*p*-tolylthiourea (dpttu), *sym*-di-*o*-anisylthiourea (doatu) and *sym*-di-α-naphthylthiourea (dαntu) with $W(CO)_6$ have been performed both by reflux and ultra-violet irradiation methods in which only monosubstituted products $[(L)W(CO)_5]$ are obtained. Several mixed ligand tungsten carbonyl derivatives, *viz.*, [(*o*-phen or 2,2'-bipy)$(L)W(CO)_3$] and [(Ph_3P or Ph_3As)$(L)W(CO)_4$] have also been synthesized. Halogenation of $[(L)W(CO)_5]$ yielded *heptacoordinated* $[(L)W(CO)_4X_2]$ (X = Br or I). The complexes have been characterized by microanalytical data, conductivity and IR measurements. The C-O stretching force constants and CO-CO stretch-stretch interaction constants of $[(L)W(CO)_5]$ derivatives have also been evaluated from the IR spectra.

Key words: Tungsten Carbonyl, Diarylthiourea Ligands, C-O Force Constants

Introduction

There has been considerable study of the ligand behaviour of sulphur donors like dialkyl- or diarylsulphides [1], dialkyl- or di(alkylthio)alkanes [2], 2-thiouracil [3], thioaldehydes [4], dialkyldisulphides [5], dithiophosphines [6], dialkyldithiocarbamates [7], thioethers [8], thioureas [9,10], dithiolenes [11] *etc.* in the displacement of CO in metal carbonyls. Thiophene, benzo- and dibenzothiophene substituted metal carbonyl derivatives found to be useful in the hydrodesulphurisation process of petroleum based feed stocks and important for both environmental and industrial reasons, have also been synthesized [12]. Substituted thioureas have not been exploited to an appreciable extent in the CO displacements of group VI B metal carbonyls.

In continuation to our recent publication [13] on Schiff base derivatives of tungsten carbonyl we describe here a study of the ligand behaviour of five symmetrically disubstituted arylthioureas (L), *viz.*, *sym*-diphenylthiourea (dptu), *sym*-di-*o*-tolylthiourea (dottu), *sym*-di-*p*-tolylthiourea (dpttu), *sym*-di-*o*-anisylthiourea (doatu) and *sym*-di-α-naphthylthiourea (dαntu) in the substitution reactions of tungsten hexacarbonyl employing both reflux and ultra-violet irradiation methods. Reactions of these donors with [(*o*-phen or 2,2'-bipy)$W(CO)_4$], [(Ph_3P or Ph_3As)$W(CO)_5$] and halogen oxidation of $[(L)W(CO)_5]$ have also been investigated.

Bonding properties of these *sym*-diarylthioureas have been interpreted by measurement of IR spectra of synthesized substituted tungsten carbonyls. The C-O stretching force constants and CO-CO stretch-stretch interaction constants have also been evaluated.

Experimental Section

All reactions and isolation procedures were carried out under argon or *in vacuo*. The *sym*-diarylthiourea ligands, [(*o*-phen or 2,2'-bipy)$W(CO)_4$] and [(Ph_3P or Ph_3As)$W(CO)_5$] have been prepared by the standard procedures given in the literature [14 – 16]. The purity of these compounds was checked by TLC and m. p. determination. All the chemicals and solvents used were of AR grade. Tungsten hexacarbonyl (Fluka) was used as such. The UV lamp (30 W) used was made by Philips Co. Holland. IR spectra were recorded on Beckman (Acculab 9) and Perkin-Elmer FT-IR (model RX I) spectrophotometers in KBr discs. Halogen contents were estimated gravimetrically by precipitation as silver salts.

Details of the preparation of representative compounds are given below. The data for other compounds are given in Table 1.

Preparation of pentacarbonyl(sym-diphenylthiourea) tungsten(0) Reflux method

Hexacarbonyltungsten(0) (0.70 g, 2 mmol) and *sym*-diphenylthiourea (0.45 g, 2 mmol) were refluxed in toluene

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Table 1. Analytical data of complexes (R/I = Reflux/Irradiation).

Complex	R/I time (h)	Yield (%)	Found (calcd.) (%)				Br or I	Complex	R/I time (h)	Yield (%)	Found (calcd.) (%)				Br or I
			C	H	N	S					C	H	N	S	
[(dottu)W(CO)$_5$]	4.5/25	82.4	41.1 (41.3)	2.8 (2.7)	4.8 (4.8)	5.3 (5.5)	–	[(dpttu)W(CO)$_5$]	4.5/25	84.2	41.2 (41.3)	2.7 (2.7)	4.7 (4.8)	5.4 (5.5)	–
[(doatu)W(CO)$_5$]	5/30	78.6	39.4 (39.2)	2.6 (2.6)	4.6 (4.5)	5.0 (5.2)	–	[(dαntu)W(CO)$_5$]	5/30	80.6	48.0 (47.8)	2.5 (2.4)	4.3 (4.2)	4.8 (4.9)	–
[(dottu)(Ph$_3$P)W(CO)$_4$]	5	68.4	54.7 (54.5)	3.7 (3.8)	3.5 (3.4)	3.8 (3.9)	–	[(dpttu)(Ph$_3$P)W(CO)$_4$]	4.5	70.5	54.6 (54.5)	3.7 (3.8)	3.4 (3.4)	3.7 (3.9)	–
[(doatu)(Ph$_3$P)W(CO)$_4$]	5	66.3	54.6 (54.4)	3.6 (3.6)	3.3 (3.3)	3.5 (3.7)	–	[(dαntu)(Ph$_3$P)W(CO)$_4$]	5	69.4	58.0 (58.2)	3.5 (3.4)	3.0 (3.1)	3.6 (3.6)	–
[(dptu)(Ph$_3$As)W(CO)$_4$]	5	76.6	50.4 (50.6)	3.1 (3.2)	3.3 (3.3)	3.6 (3.8)	–	[(dottu)(Ph$_3$As)W(CO)$_4$]	5	70.2	51.4 (51.7)	3.6 (3.6)	3.1 (3.2)	3.5 (3.7)	–
[(dpttu)(Ph$_3$As)W(CO)$_4$]	5	67.0	51.6 (51.7)	3.4 (3.6)	3.2 (3.2)	3.5 (3.7)	–	[(doatu)(Ph$_3$As)W(CO)$_4$]	5.5	68.3	49.6 (49.8)	3.3 (3.4)	3.0 (3.1)	3.4 (3.5)	–
[(dαntu)(Ph$_3$As)W(CO)$_4$]	5	71.4	55.2 (55.4)	3.2 (3.3)	3.0 (3.0)	3.2 (3.4)	–	[(dottu)(2,2’-bipy)W(CO)$_3$]	4	76.4	49.1 (49.4)	3.4 (3.5)	8.3 (8.2)	4.7 (4.7)	–
[(dpttu)(2,2’-bipy)W(CO)$_3$]	3.5	78.1	49.3 (49.4)	3.5 (3.5)	8.0 (8.2)	4.5 (4.7)	–	[(doatu)(2,2’-bipy)W(CO)$_3$]	4.5	70.0	47.2 (47.1)	3.4 (3.3)	7.6 (7.8)	4.3 (4.4)	–
[(dαntu)(2,2’-bipy)W(CO)$_3$]	4	72.6	54.1 (54.2)	3.2 (3.1)	7.5 (7.4)	4.0 (4.2)	–	[(dptu)(*o*-phen)W(CO)$_3$]	4	80.2	49.4 (49.7)	2.8 (2.9)	8.3 (8.2)	4.5 (4.7)	–
[(dottu)(*o*-phen)W(CO)$_3$]	4	78.3	50.9 (51.1)	3.3 (3.4)	7.7 (7.9)	4.4 (4.5)	–	[(dpttu)(*o*-phen)W(CO)$_3$]	3.5	77.3	51.0 (51.1)	3.2 (3.4)	8.0 (7.9)	4.4 (4.5)	–
[(doatu)(*o*-phen)W(CO)$_3$]	4.5	69.8	48.6 (48.9)	3.1 (3.2)	7.5 7.6	4.1 (4.3)	–	[(dαntu)(*o*-phen)W(CO)$_3$]	4	74.3	55.4 (55.6)	2.9 (3.0)	7.2 (7.2)	3.9 (4.1)	–
[(dottu)W(CO)$_4$I$_2$]	–	61.4	28.1 (28.3)	1.9 (2.0)	3.5 (3.4)	3.8 (3.9)	32.1 (31.4)	[(dpttu)W(CO)$_4$I$_2$]	–	58.6	28.6 (28.3)	2.1 (2.0)	3.4 (3.4)	3.8 (3.9)	32.6 (31.4)
[(doatu)W(CO)$_4$I$_2$]	–	57.3	27.6 (27.2)	2.0 (1.9)	3.4 (3.3)	3.8 (3.7)	31.1 (30.2)	[(dαntu)W(CO)$_4$I$_2$]	–	59.2	33.8 (34.1)	1.9 (1.8)	3.2 (3.1)	3.5 (3.6)	29.2 (28.9)
[(dptu)W(CO)$_4$Br$_2$]	–	52.4	24.2 (24.8)	1.6 (1.7)	4.2 (4.1)	4.8 (4.7)	24.2 (23.3)	[(dottu)W(CO)$_4$Br$_2$]	–	51.2	31.8 (32.1)	2.1 (2.2)	3.8 (3.9)	4.4 (4.5)	23.1 (22.4)
[(dpttu)W(CO)$_4$Br$_2$]	–	54.6	31.9 (32.1)	2.1 (2.2)	3.8 (3.9)	4.5 (4.5)	23.2 (22.4)	[(doatu)W(CO)$_4$Br$_2$]	–	56.2	30.2 (30.6)	2.2 (2.1)	3.8 (3.7)	4.9 (4.8)	22.2 (21.5)
[(dαntu)W(CO)$_4$Br$_2$]	–	53.1	38.6 (38.3)	2.0 (2.1)	3.4 (3.5)	4.2 (4.1)	21.2 (20.3)								

Table 2. CO stretching frequencies with modes and CO force constants of [(L)W(CO)$_5$] complexes.

Complex	v(co) (cm^{-1})		Force constant (mdynes/Å)		
			k$_1$	k$_2$	k$_i$
[(dptu)W(CO)$_5$]	2070m (A$_1$), 1920s (E),	1974s (B$_1$), 1896m (A$_1$)	14.76	15.73	0.42
[(dottu)W(CO)$_5$]	2069m (A$_1$), 1918s (E),	1972s (B$_1$), 1893m (A$_1$)	14.71	15.70	0.42
[(dpttu)W(CO)$_5$]	2070m (A$_1$), 1920s (E),	1970s (B$_1$), 1895m (A$_1$)	14.72	15.67	0.39
[(doatu)W(CO)$_5$]	2060m (A$_1$), 1922s (E),	1973s (B$_1$), 1898 (A$_1$)	14.77	15.71	0.40
[(dαntu)W(CO)$_5$]	2065m (A$_1$), 1925s (E),	1975s (B$_1$), 1898 (A$_1$)	14.77	15.75	0.39

(25 cm^3) for 4 h. A yellowish-brown stable solid was obtained by cooling the reaction mixture and evaporating the solvent *in vacuo*. Unreacted reactants were removed by washing the residue with petroleum ether (40 – 60 °C). The product was recrystallized from benzene. It was characterized as [(PhNHCSNHPh)W(CO)$_5$] (yield: 0.89 g, 80.9%). $C_{18}H_{12}N_2O_5SW$ (552 g mol^{-1}): calcd. C 39.1, H 2.1, N 5.0, S 5.7; found C 39.3, H 2.2, N 5.0, S 5.6.

UV irradiation method

Hexacarbonyltungsten(0) (0.70 g, 2 mmol) and *sym*-diphenylthiourea (0.45 g, 2 mmol) were irradiated by UV light in tetrahydrofuran (30 cm^3) for 25 h. The colour of the mixture became deep yellow after 10 h. After another 15 h, the colour of the reaction mixture changed to brown. The mixture was cooled, and the solvent was removed *in vacuo*. Workup for the isolation of the product was identical to the reflux method.

Preparation of (2,2’-bipyridine)tricarbonyl(sym-diphenylthiourea)tungsten(0)

A mixture of (2,2’-bipyridine)tetracarbonyltungsten(0) (1.06 g, 2 mmol) and *sym*-diphenylthiourea (0.45 g, 2 mmol) was refluxed in xylene (40 cm^3). The colour of the reaction mixture deepened to violet–red in 1 h but the mixture was refluxed up to 4 h when a considerable amount of crystals settled at the bottom of the flask. The solution was cooled to r.t. and filtered. The crystalline solid was washed with petroleum ether (40 – 60 °C) and 2 – 3 times with benzene to remove unreacted reactants. It was dried *in vacuo*. [(PhNHCSNHPh)($C_{10}H_8N_2$)W(CO)$_3$] (yield 1.03 g, 78.3%). $C_{26}H_{20}N_4O_3SW$ (652 g mol^{-1}): calcd. C 47.8; H 3.0; N 8.5; S 4.9; found C 48.0; H 3.0; N 8.6; S 4.7.

Preparation of tetracarbonyl(sym-diphenylthiourea)-(triphenylphosphine)tungsten(0)

Pentacarbonyl(triphenylphosphine)tungsten(0) (1.17 g, 2 mmol) and *sym*-diphenylthiourea (0.45 g; 2 mmol) were refluxed in xylene (25 cm^3) for 5 h. The solution was cooled to r.t. and a yellow-brown solid was recovered by evaporating the solvent under *vacuo*. The unreacted reactants were removed by washing the residue 4 – 5 times with petroleum ether (40 – 60 °C). The solid was dried *in vacuo*. [(PhNHCSNHPh)(Ph$_3$P)W(CO)$_4$] (yield: 1.13 g, 72.0%). $C_{35}H_{27}N_2O_4PSW$ (786 g mol^{-1}): calcd. C 53.4; H 3.4; N 3.5; S 3.9; found C 53.1; H 3.3; N 3.6; S 3.8.

Preparation of tetracarbonyl(sym-diphenylthiourea)diiodotungsten(II)

A hexane solution of iodine (0.10 g in 30 cm^3) was added dropwise to a solution of pentacarbonyl(*sym*-diphenylthiourea)tungsten(0) (0.22 g in 10 cm^3 benzene) at r.t. with constant stirring. The colour of the iodine solution disappeared during the addition and an orange precipitate settled at the bottom of the reaction flask. The supernatant liquid was decanted and the precipitate was washed repeatedly with hexane to remove unreacted iodine. The solid was again dissolved in the minimum amount of benzene (5 cm^3) and reprecipitated by adding hexane (40 cm^3). The precipitate was dried *in vacuo*. [(PhNHCSNHPh)W(CO)$_4$I$_2$] (yield: 0.21 g, 68.0%). $C_{17}H_{12}N_2O_4SI_2W$ (778 g mol^{-1}): calcd. C 26.2; H 1.5; N 3.6; S 4.1; I 32.4; found C 26.3; H 1.6; N 3.6; S 4.2; I 32.8.

Results and Discussion

Five *sym*-diarylthioureas (L) were found to react with tungsten hexacarbonyl to give the corresponding pentacarbonyl derivatives, [(L)W(CO)$_5$] (yield : 78.6 – 84.2%). Repeated attempts to achieve a second substitution by prolonged refluxing or ultra-violet irradiation were unsuccessful and not more than one CO group could be replaced. These derivatives were yellowish-brown solids, insoluble in petroleum ether (all fractions) or hexane and dissolved in benzene, dichloromethane, chloroform, acetone, tetrahydrofuran and dimethylformamide.

Table 3. CO stretching frequencies of mixed ligand derivatives.

Complex	v (CO) (cm^{-1})			
[(dptu)(Ph$_3$P)W(CO)$_4$]	1957 w,	1905 s,	1817 s,	1790 m
[(dottu)(Ph$_3$P)W(CO)$_4$]	1962 w,	1910 s,	1830 s,	1793 m
[(dpttu)(Ph$_3$P)W(CO) $_4$]	1965 w,	1910 s,	1830 s,	1793 m
[(doatu)(Ph$_3$P)W(CO)$_4$]	1963 w,	1907 s,	1822 s,	1800 m
[(dαntu)(Ph$_3$P)W(CO)$_4$]	1961 w,	1905 s,	1830 s,	1800 m
[(dptu)(Ph$_3$As)W(CO)$_4$]	1955 w,	1902 s,	1815 s,	1788 m
[(dottu)(Ph$_3$As)W(CO)$_4$]	1958 w,	1905 s,	1822 s,	1785 m
[(dpttu)(Ph$_3$As)W(CO)$_4$]	1958 w,	1900 s,	1818 s,	1785 m
[(doatu)(Ph$_3$As)W(CO)$_4$]	1960 w,	1902 s,	1820 s,	1792 m
[(dαntu)(Ph$_3$As)W(CO)$_4$]	1957 w,	1901 s,	1820 s,	1788 m
[(dptu)(2,2^I -bipy)W(CO)$_3$]	1890 s,	1781 s,	1746 s	
[(dottu)(2,2^I -bipy)W(CO)$_3$]	1886 s,	1775 s,	1746 s	
[(dpttu)(2,2^I -bipy)W(CO)$_3$]	1892 s,	1790 s,	1743 s	
[(doatu)(2,2^I -bipy)W(CO)$_3$]	1885 s,	1778 s,	1740 m	
[(dαntu)(2,2^I -bipy)W(CO)$_3$]	1900 s,	1775 s,	1750 s	
[(dptu)(*o*-phen)W(CO)$_3$]	1897 s,	1785 s,	1742 s	
[(doatu)(*o*-phen)W(CO)$_3$]	1894 s,	1792 s,	1740 s	
[(dpttu)(*o*-phen)W(CO)$_3$]	1893 s,	1800 s,	1755 s	
[(doatu)(*o*-phen)W(CO)$_3$]	1890 s,	1796 s,	1753 s	
[(dαntu)(*o*-phen)W(CO)$_3$]	1900 s,	1796 s,	1753 m	

The IR spectra of the complexes indicated that the *sym*-diarylthiourea molecules are attached to the tungsten *via* the sulphur atom. A strong absorption of the parent diarylthioureas at ∼ 1075 cm^{-1} is very much weaker or even disappears on complex formation. This observation can be explained by the considerable change in the nature of the N-C bond, as well as C=S bond, on coordination of *sym*-diarylthioureas through the sulphur atom. A lowering of ∼ 30 cm^{-1} observed for the band near ∼ 730 cm^{-1} may be attributed to the reduced double bond character of the C=S bond.

Complexes of type [(L)W(CO)$_5$] must have local C_{4v} symmetry due to which there should be three IR active C-O stretching bands assigned to $2A_1 + E$ modes, but the IR spectra of the complexes exhibited four C-O stretching bands in the ranges 2060 – 2070, 1970 – 1975, 1918 – 1925, 1893 – 1898 cm^{-1} (Table 2). Bands in the range 2060 – 2070 cm^{-1} arise from the A_1 mode of the trans pair of carbonyl groups and bands in the range 1918 – 1925 cm^{-1} may be due to E mode whereas bands of the range 1893 – 1898 cm^{-1} can be assigned to the A_1 mode of *cis*-carbonyls. Bands due to B_1 mode (1970 – 1975 cm^{-1}) which are Raman active are also visible in the IR spectra of all the complexes because the structure of the *sym*-diarylthiourea ligands interferes with the perfect C_{4v} symmetry. Assignments of all these bands have been made on the basis of work done by Orgel [17], Cotton and Kraihanzel [18].

The C-O stretching force constants k_1 and k_2 *i.e.*, force constants of the CO groups *cis* and *trans* to the diarylthiourea substituent, respectively, and k_i, the CO-CO interaction constants have been calculated by Cotton and Kraihanzel's secular equations [18]. The values of k_1, k_2 and k_i for these derivatives have been found in the ranges 14.71 – 14.77, 15.67 – 15.75 and 0.39 – 0.42 mdynes/Å, respectively. These values confirm the validity of the vibrational mode assignments, and the results are in excellent agreement with Cotton and Kraihanzel's analyses. The C-O stretching frequencies and C-O force constants in these complexes are slightly higher as compared to metal pentacarbonyls with nitrogen donor ligands [19, 20] and lower than other derivatives containing alkyl or aryl sulphides as ligands [5, 21]. These data clearly indicate that the sulphur atom in the *sym*-diarylthioureas functions as a significant π-acceptor, but substantially less than the sulphur atom in other ligands such as alkyl or arylsulphides.

Mixed ligand derivatives of the type *cis*-[(L-L)-(L)W(CO)$_3$] (L-L=*o*-phen or 2,2'-bipy, L = *sym*-diarylthioureas) were obtained by refluxing equimolar mixtures of [(L-L)W(CO)$_4$] and *sym*-diarylthioureas in xylene for ~ 4 h. Not more than one CO group could be displaced even by employing a large excess of *sym*-diarylthiourea. The decreased donor behaviour of this ligand was further exhibited when *o*-phen or 2,2'-bipy displaced it from [(L)W(CO)$_5$] and ultimately formation of [(*o*-phen or 2,2'-bipy)W(CO)$_4$] took place. All the mixed ligand tricarbonyl derivatives were brown-black solids which decomposed on heating. They are insoluble in petroleum ether (all fractions), diethylether and carbon tetrachloride but dissolved in aromatic hydrocarbons, alcohols, acetone, dichloromethane, dioxane, and dimethylformamide.

The IR spectra of the complexes exhibited three strong bands in the carbonyl region according to C_S symmetry. The C-O stretching frequencies fall in the ranges 1885 – 1900, 1775 – 1790 and 1740 – 1750 cm^{-1} for 2,2'-bipy derivatives, and 1890 – 1900, 1785 – 1800 and 1740 – 1755 cm^{-1} when *o*-phen was present. These bands are assigned to A, A' and A" modes, respectively (Table 3). The frequencies of these bands are very low contrary to expectations for sulphur donor ligands. Such lowering may be attributed to the enhanced basicity of the sulphur atom due to partial delocalisation of the lone pair of electrons on the nitrogen atoms of *sym*-diarylthioureas.

Table 4. CO stretching frequencies of halogenated derivatives.

Complex	ν(co) (cm^{-1})			
[(dptu)W(CO)$_4$I$_2$]	2066m,	2010s,	1976sh,	1922s
[(dottu)W(CO)$_4$I$_2$]	2068m,	2010s,	1975sh,	1924s
[(dpttu)W(CO)$_4$I$_2$]	2065m,	2012s,	1976m,	1922s
[(doatu)W(CO)$_4$I$_2$]	2065m,	2014s,	1974sh,	1923s
[(dαntu)W(CO)$_4$I$_2$]	2066m,	2012s,	1975sh,	1925s
[(dptu)W(CO)$_4$Br$_2$]	2078m,	2016s,	1978m,	1930s
[(dottu)W(CO)$_4$Br$_2$]	2075m,	2015s,	1977sh,	1927s
[(dpttu)W(CO)$_4$Br$_2$]	2074m,	2014s,	1976m,	1930s
[(doatu)W(CO)$_4$Br$_2$]	2076m,	2018s,	1978sh,	1928s
[(dαntu)W(CO)$_4$Br$_2$]	2078m,	2018s,	1976sh,	1930s

Diarylthioureas displaced one CO group when refluxed with [(Ph$_3$P or Ph$_3$As)W(CO)$_5$] and lead to the formation of *cis*-[(Ph$_3$P or Ph$_3$As)(L)W(CO)$_4$]. All complexes were yellow-brown solids, insoluble in aliphatic hydrocarbons but dissolved in aromatic hydrocarbons, diethylether, alcohols and acetone. The IR spectra exhibited four C-O stretching bands in the ranges 1955 – 1965, 1900 – 1910, 1815 – 1830 and 1785 – 1800 cm^{-1} which have been assigned [18] due to A_1, A_2, B_1 and B_2 modes, respectively (Table 3) as expected for C_{2V} symmetry.

Halogenation of diarylthioureatungsten pentacarbonyls in benzene yielded products of stoichiometry [(diarylthiourea)W(CO)$_4$X$_2$] (X = Br, I) when treated with one equivalent of bromine or iodine in hexane solution at ambient temperature. On using an excess of bromine or iodine, unidentified sticky products were obtained. Similar reaction with chlorine seemed to take place but the products were too unstable to be isolated. The iodine complexes were more stable than their bromo analogues. All the complexes were brown or orange in colour. They were insoluble in aliphatic hydrocarbons and light petroleum (40 – 60 °C) but soluble in aromatic hydrocarbons, tetrahydrofuran, dichloromethane, acetone etc. In oxygenated solvents decomposition occurred and simultaneous evolution of carbon monoxide took place. Their dilute solutions in benzene showed no electrical conductivity. The IR spectra (Table 4) exhibited three strong bands (ranges 2065 – 2078, 2010 – 2018 and 1922 – 1930 cm^{-1}) along with one medium to shoulder band (1974 – 1978 cm^{-1}) in the C–O region when measured in KBr discs. The spectra resembled closely to those of the reported [22, 23] heptacoordinated [(amine)M$(CO)_4X_2$] (M = Mo, W) derivatives, with distorted pentagonal bipyramidal structure, in the frequencies and intensities of bands. The C–O frequencies of bromo complexes are in considerably higher regions in comparision to their iodo analogues which clearly indicate the better electron acceptor capability of bromine than iodine.

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