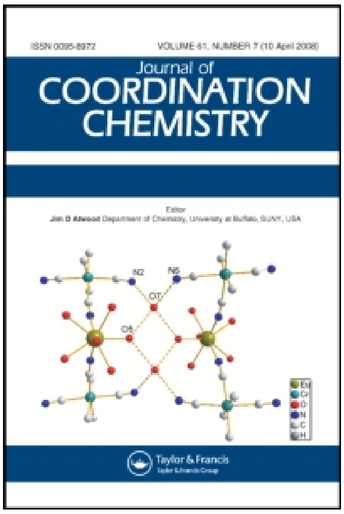

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Synthesis and characterization of tungsten carbonyl complexes containing *N*-methyl substituted urea and thiourea ligands

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Six new mixed-ligand tungsten carbonyl complexes containing *N*-methyl substituted urea and thiourea of the type $W(CO)_4[RCH_2N\text{-}(C{=}X)NH_2]$ where $X = O$ or S and R = morpholine, piperidine and diphenylamine are reported. These have been prepared by refluxing hexacarbonyl tungsten(0) with corresponding ligands in THF to produce *cis*-disubstituted products, $[(L\text{-}L)W(CO)_4]$ where L-L = a chelating bidentate ligand, morpholinomethyl urea (MMU), morpholinomethyl thiourea (MMTU), piperidinomethyl urea (PMU), piperidinomethyl thiourea (PMTU), diphenylaminomethyl urea (DAMU) and diphenylaminomethyl thiourea (DAMTU). The compounds have been characterized by elemental analysis, IR, electronic and ^{13}C NMR spectra, magnetic moments and conductivity measurements. The IR spectra suggests that in all the complexes, the ligands are bidentate chelating, coordinating the metal through carbonyl oxygen or thiocarbonyl sulphur and the ring nitrogen or *tert*-nitrogen of diphenylamine. The CO force constants and CO–CO interaction constants for these derivatives have also been calculated using Cotton–Kraihanzel secular equations, which indicate poor π-bonding ability of the ligands. ^{13}C NMR and electronic spectra reveal loss of *cis*-carbonyl ligands to produce *cis*-disubstituted tetracarbonyl derivatives. Molecular modeling studies have been carried out using Hyperchem release 7.52 which suggest a distorted octahedral geometry for these complexes.

Keywords: Tungsten carbonyl complexes; Force constants; *cis*-Configuration; Infrared spectra; C_{2v} symmetry

1. Introduction

Tungsten hexacarbonyl undergoes a variety of reactions with partial or total replacement of CO ligands [1]. These substitution reactions provide routes into much of the organometallic chemistry of tungsten. Photochemistry of tungsten carbonyl complexes, $[M(CO)_xL_{6-x}]$ has also received attention [2]. A number of derivatives of tungsten carbonyl complexes, *cis*-$[W(CO)_4L\text{-}L]$ containing diimine ligands (L-L = 2,2′-bipyridine, 1,10-phenanthroline, 1,4-diazabutadiene and pyridylamine Schiff base) have been reported [3–7]. Tungsten carbonyl complexes derived from dianions of 2-aminophenol and 1,2-diaminobenzene stabilized by π-donation from the amido groups of chelating ligands have also been reported [8].

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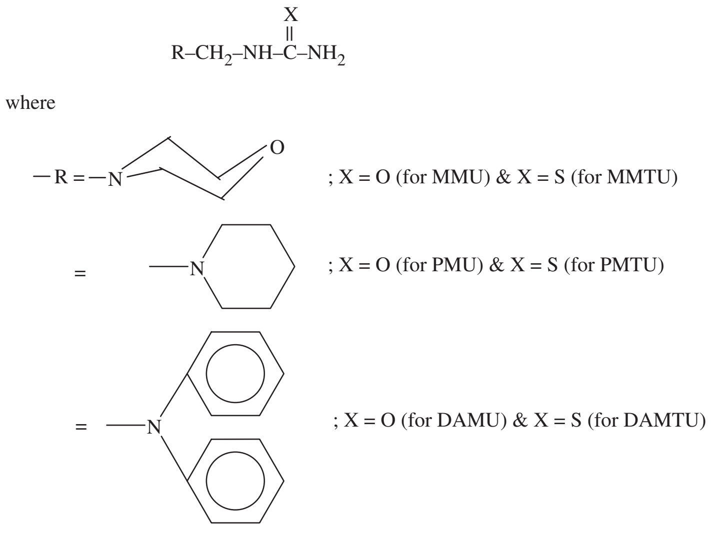
S, N-ligated derivatives of hexacarbonyltungsten(0), $[NEt_4]$ $[W(CO)_4L\text{-}L]$ (L-L = 2-thiouracilate and 6-methyl-2-thiouracilate] have been synthesized from reaction of photogenerated $W(CO)_5$(solvent) (solvent = MeOH or THF) and corresponding $[Et_4N]$ [thiouracilate] [9]. Novel orotic acid derivatives of tungsten carbonyl, $[Et_4N]_2$ $[W(CO)_4(\text{orotate})]$, $[Et_4N]_2[W(CO)_4(\text{dihydroorotate})]$ [where orotate = $(C_5H_2O_4N_2)^{2-}$, dihydro orotate = $(C_5H_4O_4N_2)^{2-}$] have been reported and found to be O,N-ligated complexes [10, 11].

Electrochemical and spectroscopic studies of tungsten carbonyl complexes containing nitrogen and phosphorus ligands, $[W(CO)_4(\text{bipy})]$, $[W(CO)_3(\text{bipy})(\text{dppm})]$ and $[W(CO)_3(\text{bipy})(\text{dppf})]$ (where bipy = 2,2′-bipyridine, dppm = *bis*(diphenylphosphino) methane, dppf = 1,1′-*bis*(diphenylphosphino)ferrocene have been carried out [12]. Amino acid derivatives of tungsten carbonyl e.g. $[W(CO)_4(O_2CCH_2NH_2)]^-$ and $[W(CO)_4(O_2CCH_2NHMe)]^-$ are stable and even crystallographically characterizable as a consequence of the π-donating ability of the amido ligands [13].

Schiff bases (SB) viz, 1,2-*bis*(4-methylbenzylideneimine) propane; 1,2-*bis*(4-methoxybenzylideneimine)propane and 1,2-*bis*(4-*N*,*N*-dimethylaminobenzylideneimine) react with tungsten carbonyl in xylene to give *cis*-disubstituted derivatives, *cis*-$[(SB)W(CO)_4]$ [14]. Halogen oxidation of these *cis*-disubstituted products has also been carried out with Cl_2, which invariably displaced all the CO groups to give $[(SB)WCl_4]$.

Complexes of morpholinomethyl urea and related ligands with divalent transition metals viz Co(II) and Cu(II) and some rare earth metals have been extensively studied for their bonding, thermal and magnetic behaviour [15–17]. In this article we have used morpholinomethyl urea (MMU), morpholinomethyl thiourea (MMTU), piperidinomethyl urea (PMU), piperidinomethyl thiourea (PMTU), diphenylaminomethyl urea (DAMU), diphenylaminomethyl thiourea (DAMTU) in CO displacement reactions of $W(CO)_6$, yielding *cis*-disubstitued products, $[(L\text{-}L)W(CO)_4]$ where L-L = MMU or related ligands.



$$R\text{–}CH_2\text{–}NH\text{–}\overset{\overset{\displaystyle X}{\|}}{C}\text{–}NH_2$$

Scheme 1. Schematic view of $[RCH_2NH\text{–}(C{=}X)\text{–}NH_2]$.

2. Experimental

2.1. *Reagents and reaction conditions*

Morpholine (Fluka) and piperidine (SDS) and diphenylamine (Fluka) were purified by distillation after keeping these bases over potassium hydroxide overnight. Urea (Merk), thiourea (Ranbaxy), diphenylamine (Fluka) formaldehyde (Qualigens), THF (Ranbaxy) and tungsten hexacarbonyl (Aldrich) were used as supplied. The ligands were prepared by reported methods [18] (Scheme 1). All reactions were carried out under dry conditions in an atmosphere of nitrogen.

2.2. *Preparation of [W(CO)$_4$(L-L)]*

Complexes **1**–**6** were obtained according to the following general method.

$W(CO)_6$ (1.05 g, 3 mmol) and the ligand (3 mmol): MMU (0.477 g), MMTU (0.525 g), PMU (0.471 g), PMTU (0.519 g), DAMU (0.723 g) and DAMTU (0.771 g) were refluxed in 50 cm^3 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: 65–80%). Analytical data, colour and melting point of the complexes are listed in table 1.

2.3. *Physical methods*

Analysis of tungsten was carried out gravimetrically by the reported method [19]. Carbon, hydrogen, nitrogen and sulphur were analysed micro-analytically. Molar conductivity in DMF at room temperature was measured by an Elico conductivity bridge type CM82T using a conductivity cell with a cell constant of 0.74. IR spectra of complexes over the region 4000–400 cm^{-1} were recorded on a Vector-22 FT-IR spectrophotometer using KBr discs. Electronic spectra were run in DMSO on a

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

Complex (Empirical formula)	Colour	M.p. (°C)	Found (Calcd)%					Λ_M
			C	H	N	S	W	(Ω cm^2 mol^{-1})
[W(CO$_4$)MMU]	Light yellow	125	26.30	2.83	9.21	–	40.22	18
($WC_{10}H_{13}N_7O_5S$, 455.03) (**1**)			(26.37)	(2.85)	(9.23)		(40.40)	
[W(CO$_4$)MMTU]	Light yellow	128	25.41	2.73	8.80	6.61	38.98	16
($WC_{10}H_{13}N_3O_6$, 455.03) (**2**)			(25.47)	(2.75)	(8.91)	(6.71)	(39.02)	
[W(CO$_4$)PMU]	Yellow	120	28.92	3.21	9.17	–	40.35	25
($WC_{11}H_{15}N_3O_5$, 453.04) (**3**)			(29.13)	(3.31)	(9.27)		(40.57)	
[W(CO$_4$)PMTU]	Light yellow	126	28.10	3.20	8.89	6.68	39.10	21
($WC_{11}H_{15}N_3O_4S$, 469.00) (**4**)			(28.14)	(3.19)	(8.95)	(6.82)	(39.01)	
[W(CO$_4$)DAMU]	Light yellow	133	40.20	2.75	7.75	–	34.13	30
($WC_{18}H_{15}N_3O_5$, 537.07) (**5**)			(40.21)	(2.79)	(7.82)		(34.23)	
[W(CO$_4$)DAMTU]	Light yellow	141	38.98	2.73	7.46	5.72	33.22	24
($WC_{18}H_{15}N_3O_4S$, 553.07) (**6**)			(39.05)	(2.71)	(7.59)	(5.78)	(33.23)	

Beckman Du-6 spectrophotometer in the 190–800 nm range. ^{13}C NMR spectra were obtained on a Brucker spectrometer with reference to residual solvent peaks and TMS. Magnetic measurements at room temperature were carried out by Gouy's method using $Hg[Co(SCN)_4]$ as the calibrant.

3. Results and discussion

The analytical and spectroscopic results (tables 1–4) showed that all the complexes are mononuclear with general formula *cis*-$[(L\text{-}L)W(CO)_4]$ where L-L = MMU, MMTU, PMU, PMTU, DAMU and DAMTU. All the complexes are light yellow, air stable solids with characteristic melting points and soluble in DMF, DMSO and THF but insoluble in *n*-hexane and light petroleum.

3.1. *IR spectra*

The IR spectra (table 2) of all the complexes show four CO stretching bands in the infrared region 2057–1900 cm^{-1} due to $2A_1 + B_1 + B_2$ modes as expected for C_{2v} symmetry and in agreement with their *cis*-configuration [20]. 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 CO force constants and CO–CO interaction constants for these derivatives have been calculated using Cotton–Kraihanzel secular equations [20].

$$2A_1 \begin{vmatrix} \mu(k_2 + 2k_i) - \lambda & 2\mu k_i \\ 2\mu k_i & \mu(k_1 + k_i) - \lambda \end{vmatrix} = 0 \tag{1}$$

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

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

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

	ν(C=Z) Z = O or S	ν(C–N–C)	ν(CO)				Force constant (mdynes Å^{-1})		
Complex	Complex (ligand)	Complex (ligand)	A_1 *trans*	B_1	A_1 *cis*	B_2	k_1	k_2	k_i
$[W(CO)_4MMU]$ (**1**)	1635 (1655)	1144 (1165) 1120 (1140)	2057	1963	1952	1945	15.49	16.04	0.31
$[W(CO)_4MMTU]$ (**2**)	1278 (1295)	1142 (1162) 1116 (1135)	2050	1961	1944	1934	15.39	16.10	0.29
$[W(CO)_4PMU]$ (**3**)	1638 (1660)	1138 (1150) 1110 (1120)	2052	1961	1947	1938	15.45	16.10	0.29
$[W(CO)_4PMTU]$ (**4**)	1284 (1310)	1140 (1160) 1105 (1120)	2054	1961	1945	1934	15.41	16.14	0.31
$[W(CO)_4DAMU]$ (**5**)	1634 (1655)	1136 (1160) 1110 (1135)	2075	1962	1957	1946	15.60	16.10	0.31
$[W(CO)_4DAMTU]$ (**6**)	1264 (1285)	1135 (1160) 1104 (1140)	3385	1955	1944	1940	15.50	16.05	0.31

Table 3. Electronic spectral data of *cis*-[(L-L)W(CO)$_4$] complexes.

Complex	λ_{max}[a] (d–π* CO transition)			λ_{max}[a] (d–d transition)
[W(CO)$_4$MMU] (**1**)	32051 (1930)	34722 (2005)	35205 (2117)	21900 (324)
[W(CO)$_4$MMTU] (**2**)	32000 (1925)	34965 (1998)	35613 (2270)	22763 (334)
[W(CO)$_4$PMU] (**3**)	32568 (1934)	34722 (2215)	35714 (2268)	21925 (350)
[W(CO)$_4$PMTU] (**4**)	32460 (1990)	34720 (2260)	35744 (2170)	27865 (325)
[W(CO)$_4$DAMU] (**5**)	32200 (1870)	34843 (1937)	35505 (2270)	28900 (278)
[W(CO)$_4$DAMTU] (**6**)	32063 (2050)	34715 (1970)	35335 (2330)	26800 (380)

[a]Figures in the parenthesis indicate molar extinction coefficient values in $1\,cm^{-1}\,mol^{-1}$.

Table 4. ^{13}C NMR data[a] for the carbonyl ligands in [W(CO)$_4$(L-L) complexs.

Complex	CO-(axial)	^{13}C resonance (ppm) CO-(*trans* to S or O)	CO-(*trans* to N)
[W(CO)$_4$MMU] (**1**)	197.84	212.20	212.80
[W(CO)$_4$MMTU] (**2**)	197.29	215.45	214.06
[W(CO)$_4$PMU] (**3**)	200.54	216.05	216.75
[W(CO)$_4$PMTU] (**4**)	200.24	215.48	214.05
[W(CO)$_4$DAMU] (**5**)	204.61	218.04	218.21
[W(CO)$_4$DAMTU] (**6**)	204.31	216.71	214.85

[a]Solvent: DMSO.

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 constants, 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}. The values of k_1, k_2 and k_i were found in the ranges 15.39–15.60, 16.04–16.14 and 0.29–0.31 mdynes Å^{-1} respectively, which confirms the vibrational mode assignments. The values of CO stretching force constants in the complexes are lower than that for W(CO)$_6$ (16.41 mdynes Å^{-1}) indicating the replacement of two CO groups by poor π-bonding ligands (L-L) [21, 22]. These values are close to the values of force constants deduced for other nitrogen containing *cis*-disubstituted group VI metal carbonyls [23, 24].

Moreover, the ν(C=O) absorption band at 1655–1660 cm^{-1} in the free ligands MMU, PMU and DAMU and ν(C=S) modes of MMTU, PMTU and DAMTU at 1295–1310 and 770–785 cm^{-1} (table 2) are lowered by 20–30 cm^{-1} in the complexes indicating involvement of carbonyl oxygen (O) or thiocarbonyl sulphur (S) in bonding with tungsten. The ν(C–N–C) mode of morpholine and piperidine ring (for **1** to **4**) and ν(C–N–C) of diphenylamine around 1120–1165 cm^{-1} show a negative shift in the complexes indicating involvement of the ring nitrogen (in case of **1** to **4**) and tertiary nitrogen (for **5** and **6**) in bonding with tungsten. A slight positive shift in (C–O–C) stretching mode of morpholine ring shows that morpholine ring does not bond with tungsten.

These IR bands suggest that in all the complexes the ligands are bidentate chelating, coordinating the metal through carbonyl (O) or thio carbonyl (S) and the ring nitrogen [in case of complexes **1** to **4**].

3.2. *Conductance and magnetic measurements*

The observed molar conductance of these complexes in THF (10^{-3} M) is in the range 16–30 $\Omega\,cm^2\,mol^{-1}$, which indicates the non-electrolytic nature of the complexes. All the complexes were found to be diamagnetic as expected for low spin tungsten(0) complexes.

3.3. *Electronic spectra*

Electronic spectra of mixed-ligand carbonyl derivatives of the type *cis*-$M(CO)_4L_2$ ($M = Cr$, Mo, W and $L_2 =$ a bidentate nitrogen ligand) have been extensively studied by Stufkens and collaborators [25, 26]. Of primary interest are the enhanced (Raman) vibrations coupled to the M–L MLCT transitions.

In these C_{2v} compounds, the degeneracy of the t_{2g} level is totally lost and three transitions lie under the MLCT band envelope. The complexes under study exhibit three sharp spectral peaks in the region of 32051–35744 cm^{-1}, attributed to d–π* co transitions. A peak of low intensity in the region of 21900–28900 cm^{-1}, which may be assigned to a d–d transition is also observed.

3.4. *^{13}C NMR spectra*

^{13}C NMR spectra of **1** to **6** in DMSO (table 4) are comprised of three signals corresponding to one resonance for the two *cis* CO's and one for each of the other two CO's, *trans* to ring nitrogen and *trans* to oxygen (for complexes **1**, **3** and **5**) or sulphur (for complexes **2**, **4** and **6**). Both of these later resonances are slightly downfield (assigned to CO groups *trans* to coordinated nitrogen and oxygen or sulphur) from the more intense resonance for the two *cis* CO ligands. The assignments of the ^{13}C signals for CO groups *trans* to nitrogen *versus* those *trans* to sulphur or oxygen are based on general observation that ^{13}C resonances for the better donor group is in general upfield relative to a weaker donor group in $W(CO)_4$ derivatives [27, 28]. As anticipated from the ν(CO) parameters, the ^{13}C chemical shifts of the CO ligands for the more electron donating O, N-ligated complexes are further downfield than the corresponding parameters for the S, N-ligated derivatives. Similar conclusions have been drawn from ^{13}C chemical shifts of the CO ligands in complex anion, $[W(CO)_4(glycinate)]^-$ [8].

3.5. *^1H NMR spectra*

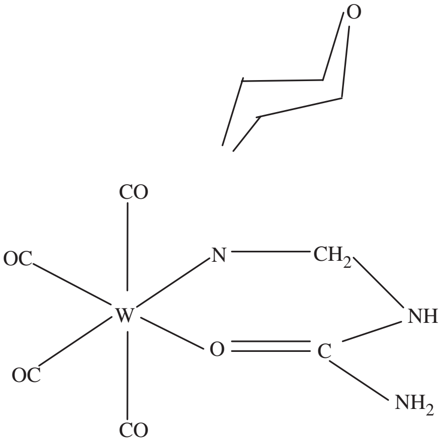
The ^1H NMR spectrum of the representative ligand, morpholinomethyl urea (MMU) was recorded in DMSO. The spectrum shows a triplet at δ 3.5 ppm for N–CH_2 of morpholine ring and a triplet at δ 3.75 ppm for CH_2–O of morpholine ring. The two methylene protons of N–CH_2–NH appear at δ 6.33 ppm as doublet. In the ^1H NMR spectrum of the complex, $[W(CO)_4MMU]$ the peaks corresponding to four protons of $-CH_2$ groups of $N{-}CH_2$ in morpholine ring undergo downfield shift with δ 3.60 ppm. This is due to coordination of ring nitrogen of morpholine with tungsten.

3.6. *Molecular modeling*

Since single crystals could not be grown for these complexes, it was thought worthwhile to obtain structural information through molecular modeling. The molecular modeling calculations for two representative complexes, $[W(CO)_4$ MMU] (**1**) and $[W(CO)_4$ PMU] (**3**) has been carried out using Hyperchem release 7.52 professional version that allows for rapid structural building, geometry optimization and molecular display [29].

Energy values obtained for the complexes indicate a distorted octahedral geometry. The lowest energy values obtained from these studies for the distorted octahedral complexes **1** and **3** are 26.81 and 31.36 k cal mol^{-1}, respectively. Vibrational and electronic spectra obtained by molecular modeling calculations match original spectra of the complexes thereby supporting the proposed structures for these complexes.

Based on the above observations, it is proposed that these complexes are of general composition, $[(L\text{-}L)\ W(CO)_4]$ (where L-L = MMU, MMTU, PMU, PMTU, DAMU and DAMTU). The representative structure proposed for $[W(CO)_4MMU]$ is:



(**I**)

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