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AMINETUNGSTEN CARBONYLS

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Summary

The important spectral features in several mono- and di-substituted aminetungsten carbonyls as changes take place in the nature of N—H and C—O bonds on coordination are discussed. Two N—H bands due to asymmetric and symmetric modes appear in the spectra of (amine)W$(CO)_5$ derivatives. For *cis*-(amine)$_2$W$(CO)_4$ four N—H stretching symmetrical and asymmetrical bands due to A_1 and B_1 modes have been recorded. In both the cases the frequency difference due to asymmetric modes is greater than for the symmetric modes. Furthermore, the bands due to the B_1 mode appear at lower frequency than those due to the A_1 mode. The C—O stretching force constants K_1 and K_2, of the CO groups *trans* and *cis* to the substituent nitrogen donor, respectively, and the stretch—stretch interaction constant K_i, have been deduced. Using these data the C—O bond orders and the electronic charge distributions on undisplaced CO groups have been deduced.

Introduction

We have earlier described the preparation and vibrational studies of several substituted molybdenum carbonyl derivatives [1-4]. In this paper we report the synthesis of some of the amine-substituted tungsten carbonyls and the spectral changes which occur due to change in the nature of N—H and C—O bonds on coordination. We have also evaluated the C—O bond distances, CO π bond orders, and hence, the electronic charge densities on remaining carbonyl groups in these derivatives with the help of semiempirical equations developed in this laboratory.

Results and discussion

Preparative methods are identical to those described in our earlier communication [1]. Ethylamine, isopropylamine, butylamine, benzylamine, cyclohexylamine, piperidine, morpholine and piperazine reacted with tungsten hexacarbonyl on heating in evacuated sealed tubes to give mono- and di-substituted derivatives, depending upon the temperature and time. For disubstituted derivatives the reflux method was better than heating the reactants in sealed tubes. Allylamine, α-picoline and quinoline upon reaction with $W(CO)_6$ yielded only monosubstituted derivatives. Diisopropylamine gave only monosubstituted derivative when a solution of diisopropylamine and $W(CO)_6$ in hexane was irradiated with UV light. Synthesis of tris(amine)tungsten tricarbonyls (amine = butylamine, benzylamine and cyclohexylamine) has been described elsewhere [5]. Unlike corresponding molybdenum analogues, the tungsten derivatives were fairly air-stable in the solid state, but not in solution. Aminetungsten pentacarbonyls were soluble in polar and nonpolar organic solvents but bis(amine)tungsten tetracarbonyls were practically insoluble in nonpolar solvents and sparingly soluble in polar solvents.

Infrared spectra

N—H bands. When amines coordinate to metal atoms, lowering in N—H frequencies is observed. To deduce the effect of coordination on N—H frequencies it was essential to allocate the exact positions of free N—H bands in the infrared spectra of amines. IR spectra of strong solutions of amines show several bands in the N—H stretching region, some of which, at slightly lower frequency appear to be due to bonded N—H. Such lowering corresponds to hydrogen bonding effects and hinders the exact assignment of free N—H bands. For this reason IR spectra of 0.0005 *M* solutions of all the amines were measured in CCl_4, except for isopropylamine; quinoline and α-picoline do not have N—H bonds (Table 1). Since hydrogen bonding is very small in dilute solutions it became possible to distinguish between free and hydrogen bonded N—H bands. At this low concentration only two medium weak N—H bands appeared in ethyl-, butyl-, benzyl- and cyclohexyl-amines and have been assigned as asymmetric and symmetric N—H stretching bands. These bands are in fair agreement with Bellamy's relation [6]: $\nu_{sym} = 345.5 + 0.876\ \nu_{asym}$. Diisopropylamine, piperidine, morpholine and piperazine showed a single N—H stretching band in their IR spectra. After the exact assignment of the free N—H band the net effect of

TABLE 1

N—H FREQUENCIES FOR AMINES (CCl_4, 0.0005 *M*)

Amine	ν_{asym}(N—H)	ν_{sym} (N—H)	ν(N—H)
Ethylamine	3455	3370	
Butylamine	3455	3370	
Benzylamine	3450	3365	
Cyclohexylamine	3460	3360	
Allylamine	3470	3365	
Diisopropylamine			3390
Piperidine			3350
Piperazine			3340
Morpholine			3350

coordination could be deduced. In this analysis the assumption has been made that the vibrations of amine molecules are not strongly coupled to other vibrations and that the small vibrational coupling which may be present will not cause major perturbations or splittings, and therefore the ligand vibrations can be analysed based only on the local symmetry. The $(Am)W(CO)_5$ molecules possess C_{4v} symmetry, and at least two N—H stretching bands are expected due to asymmetric and symmetric frequencies of the A_1 mode when the primary amines coordinate the metal atom, displacing only one CO group of $W(CO)_6$. In our investigations we have been able to record two N—H stretching bands. From Table 2 it is obvious that the frequency difference due to asymmetric mode is greater than the symmetric mode. It is concluded that both W—N—H bonds are equivalent and that Bellamy's relation holds for substituted derivatives also. For diisopropylaminetungsten pentacarbonyl only one N—H stretching band was observed.

The disubstituted derivatives *cis*-$(Am)_2W(CO)_4$ possess C_{2v} symmetry. Four N—H stretching symmetric and asymmetric bands due to A_1 and B_1 modes were observed, as expected. In these cases the frequency difference due to the asymmetric mode was greater than the symmetric mode. Furthermore, the band due to the B_1 mode appeared at lower frequency than that due to the A_1 mode (Table 3).

C—O bands. Due to the air-sensitive nature of solutions of these complexes the infrared spectra were measured on mulls. The assignments of C—O stretching bands of $(Am)W(CO)_5$ and *cis*-$(Am)_2W(CO)_4$ have been carried out on the basis of an analysis given by Cotton and Kraihanzel [7]. Three C—O stretching bands due to $(2A_1 + E)$ modes are expected in the IR spectra of monosubstituted derivatives. In fact four C—O bands were observed; the fourth might arise due to the B_1 mode which is Raman-active and may gain some intensity in the IR due to distortion from C_{4v} symmetry (Table 4). For disubstituted derivatives *cis*-$(Am)_2W(CO)_4$, four carbonyl stretching bands have been recorded, due to $2A_1 + B_1 + B_2$, as expected for C_{2v} symmetry (Table 4). The C—O stretching force constants K_1 and K_2, of CO groups *trans* and *cis* to the substituent nitrogen donor, respectively, and the stretch—stretch interaction constant K_i, have been deduced. Since the force constants have been calculated from frequencies of mull spectra, they can be considered a lower limit and might well be 0.10 to 0.20 units higher if obtained from solution data.

The C—O bond distances and C—O π-bond orders have been deduced from eqns. 1 and 2.

$$0.1\,F = 6.74 - 4.50\,R \qquad (1)$$

$$R = 1.38 - 0.15\,P_\pi \qquad (2)$$

(F = C—O stretching force constant, R = C—O bond distance and P_π = π-bond order)

Equation 1 has been found to be valid for a large number of compounds, and has been developed by plotting C—O stretching force constants [7-10] versus C—O bond distances [8,11,12] for nine compounds containing C=O and C≡O groups [CO, CO_2, C_3O_2, H_2CO, $W(CO)_6$, $Mo(CO)_6$, $Cr(CO)_6$, $Ni(CO)_4$ and (benzene)$Cr(CO)_3$] (Fig. 1).

(continued on p. 234)

TABLE 2

EFFECT OF COORDINATION ON N—H STRETCHING FREQUENCIES: (Am)W(CO)$_5$ DERIVATIVES

Compound	ν_{asym}(N—H)	$\Delta\nu_{asym}$(N—H)	ν_{sym}(N—H)	$\Delta\nu_{sym}$(N—H)	ν(N—H)	$\Delta\nu$(N—H)
$(C_2H_5NH_2)W(CO)_5$	3340	115	3308	62		
$(C_4H_9NH_2)W(CO)_5$	3340	115	3313	57		
$(C_6H_5CH_2NH_2)W(CO)_5$	3335	115	3298	67		
$(C_6H_{11}NH_2)W(CO)_5$	3355	105	3303	57		
$(C_3H_5NH_2)W(CO)_5$	3370	100	3310	55		
$(i\text{-}C_3H_7)_2NHW(CO)_5$					3206	94
$(C_5H_{11}N)W(CO)_5$					3265	85
$(C_4H_{10}N_2)W(CO)_5$					3255	85
$(C_4H_9NO)W(CO)_5$					3270	80

TABLE 3

EFFECT OF COORDINATION ON N—H STRETCHING FREQUENCIES: *cis*-$(Am)_2W(CO)_4$ DERIVATIVES

Compound	A_1			
	ν_{asym}(N—H)	$\Delta\nu_{asym}$(N—H)	ν_{sym}(N—H)	$\Delta\nu_{sym}$(N—H)
$(C_2H_5NH_2)_2W(CO)_4$	3340	115	3268	92
$(C_4H_9NH_2)_2W(CO)_4$	3340	115	3263	97
$(C_6H_5CH_2NH_2)_2W(CO)_4$	3315	135	3270	95
$(C_6H_{11}NH_2)_2W(CO)_4$	3330	130	3265	95

Compound	B_1			
	ν_{asym}(N—H)	$\Delta\nu_{asym}$(N—H)	ν_{sym}(N—H)	$\Delta\nu_{sym}$(N—H)
$(C_2H_5NH_2)_2W(CO)_4$	3310	145	3268	102
$(C_4H_9NH_2)_2W(CO)_4$	3290	165	3263	107
$(C_6H_5CH_2NH_2)_2W(CO)_4$	3280	170	3255	110
$(C_6H_{11}NH_2)_2W(CO)_4$	3295	165	3248	112

	ν_{av}(N—H)	$\Delta\nu_{av}$(N—H)
$(C_5H_{11}N)_2W(CO)_4$	3224	126
$(C_4H_{10}N_2)W(CO)_4$	3220	120
$(C_4H_9NO)_2W(CO)_4$	3222	128

TABLE 4

C—O FORCE CONSTANTS, AND C—O BOND LENGTHS IN MONO- AND DI-SUBSTITUTED TUNGSTEN CARBONYLS

Compound	Frequencies observed (cm^{-1})	Force constants (mdynes/Å)			C—O bond lengths (Å) (Calcd.)	
		K_1	K_2	K_i	R_1	R_2
$(C_2H_5NH_2)W(CO)_5$	2061, 1963, 1918, 1884	14.56	15.56	0.35	1.17	1.15
$(i\text{-}C_3H_7NH_2)W(CO)_5$	2062, 1965, 1915, 1884	14.54	15.58	0.39	1.17	1.15
$(i\text{-}C_3H_7)_2NHW(CO)_5$	2062, 1965, 1915, 1884	14.54	15.58	0.39	1.17	1.15
$(C_4H_9NH_2)W(CO)_5$	2062, 1961, 1918, 1884	14.51	15.54	0.34	1.17	1.15
$(C_7H_7NH_2)W(CO)_5$	2075, 1967, 1914, 1887	14.62	15.62	0.45	1.17	1.15
$(C_6H_{11}NH_2)W(CO)_5$	2075, 1967, 1914, 1887	14.59	15.61	0.41	1.17	1.15
$(C_3H_5NH_2)W(CO)_5$	2064, 1963, 1918, 1884	14.56	15.56	0.35	1.17	1.15
$(C_5H_{11}N)W(CO)_5$	2080, 1975, 1923, 1887	14.58	15.75	0.41	1.17	1.15
$(C_4H_{10}N_2)W(CO)_5$	2080, 1975, 1923, 1887	14.58	15.75	0.41	1.17	1.15
$(C_4H_9NO)W(CO)_5$	2072, 1967, 1914, 1887	14.65	15.62	0.45	1.17	1.15
$(\alpha\text{-}C_5H_4NCH_3)W(CO)_5$	2070, 1961, 1911, 1887	14.65	15.54	0.43	1.17	1.15
$(C_9H_7N)W(CO)_5$	2065, 1965, 1915, 1884	14.54	15.58	0.39	1.17	1.15
$(C_2H_5NH_2)_2W(CO)_4$	1990, 1869, 1844, 1797	13.50	14.65	0.46	1.19	1.16
$(i\text{-}C_3H_7NH_2)_2W(CO)_4$	2000, 1869, 1844, 1818	13.82	14.69	0.48	1.18	1.16
$(C_4H_9NH_2)_2W(CO)_4$	2000, 1869, 1844, 1818	13.82	14.69	0.48	1.18	1.16
$(C_7H_7NH_2)_2W(CO)_4$	2000, 1858, 1844, 1805	13.64	14.71	0.49	1.19	1.16
$(C_6H_{11}NH_2)_2W(CO)_4$	2000, 1869, 1844, 1818	13.82	14.69	0.48	1.18	1.16
$(C_5H_{11}N)_2W(CO)_4$	2000, 1865, 1844, 1814	13.59	14.72	0.49	1.19	1.16
$(C_4H_{10}N_2)W(CO)_4$	2000, 1858, 1844, 1805	13.64	14.71	0.49	1.19	1.16
$(C_4H_9NO)_2W(CO)_4$	2000, 1855, 1844, 1805	13.82	14.69	0.48	1.18	1.16

Equation 2 has been developed by plotting C—O bond orders (P_π) against C—O bond distances (R) of some of the compounds containing carbonyl groups [13] [$V(CO)_6^-$, $W(CO)_6$, $Re(CO)_6^+$, CO and $H_2(CO)$].

The validity of eqns. 1 and 2 is supported by the relation 3, developed by Cotton [14]. On combining eqns. 1 and 2 we get the relation 4, almost the same as relation 3.

$$F = 6.80\,P_\pi + 5.03 \tag{3}$$

$$F = 6.75\,P_\pi + 5.30 \tag{4}$$

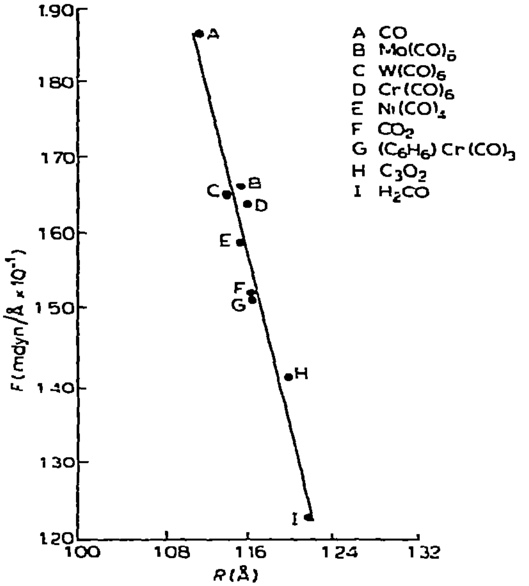

Fig. 1. A plot of C—O force constants (*F*) vs. C—O bond lengths (*R*).

After having a known CO π-bond order, electronic charge distributions (Q_{CO}) on undisplaced carbonyl groups in the substituted tungsten carbonyls have been calculated (Table 5) from eqn. 5 [15].

$$P_\pi = 2 - | Q_{CO}/2 | \qquad (5)$$

From these calculations of π-bond orders and electronic charge densities on undisplaced C—O groups, it is apparent that amine molecules affect the

TABLE 5

CO π-BOND ORDERS AND CHARGE DENSITIES[a]

Compound	CO π-bond order		CO-charge densities	
	P'_π	P''_π	Q'_{CO}	Q''_{CO}
$(C_2H_5NH_2)W(CO)_5$	1.40	1.54	−1.20	−0.92
$(i\text{-}C_3H_7NH_2)W(CO)_5$	1.40	1.54	−1.20	−0.92
$(i\text{-}C_3H_7)_2NHW(CO)_5$	1.40	1.54	−1.20	−0.92
$(C_4H_9NH_2)W(CO)_5$	1.40	1.54	−1.20	−0.92
$(C_7H_7NH_2)W(CO)_5$	1.40	1.54	−1.20	−0.92
$(C_6H_{11}NH_2)W(CO)_5$	1.40	1.54	−1.20	−0.92
$(C_3H_5NH_2)W(CO)_5$	1.40	1.54	−1.20	−0.92
$(C_5H_{11}N)W(CO)_5$	1.40	1.54	−1.20	−0.92
$(C_4H_{10}N_2)W(CO)_5$	1.40	1.54	−1.20	−0.92
$(C_4H_9NO)W(CO)_5$	1.40	1.54	−1.20	−0.92
$(\alpha\text{-}C_5H_4NCH_3)W(CO)_5$	1.40	1.54	−1.20	−0.92
$(C_9H_7N)W(CO)_5$	1.40	1.54	−1.20	−0.92
$(C_2H_5NH_2)_2W(CO)_4$	1.26	1.46	−1.48	−1.04
$(i\text{-}C_3H_7NH_2)_2W(CO)_4$	1.33	1.46	−1.34	−1.04
$(C_4H_9NH_2)_2W(CO)_4$	1.33	1.46	−1.34	−1.04
$(C_7H_7NH)_2W(CO)_4$	1.26	1.46	−1.48	−1.04
$(C_6H_{11}NH_2)_2W(CO)_4$	1.33	1.46	−1.34	−1.04
$(C_5H_{11}N)_2W(CO)_4$	1.26	1.46	−1.48	−1.04
$(C_4H_{10}N_2)W(CO)_4$	1.26	1.46	−1.48	−1.04
$(C_4H_9NO)_2W(CO)_4$	1.33	1.46	−1.34	−1.04

[a] P'_π and Q'_{CO} denote the respective parameters for *trans*-CO, and P''_π and Q''_{CO} for *cis*-CO.

TABLE 6. PREPARATION AND ANALYTICAL DATA

Compound	Method	Reaction conditions	Characteristics M.p. (°C)	Yield (%)	Analysis found (calcd.)(%)		
					C	H	N
$(C_2H_5NH_2)_2W(CO)_4$	Sealed tube	125°/10h	Golden-yellow crystals 220 (dec.)	78.5	24.7 (24.8)	3.4 (3.6)	7.2 (7.2)
$(i\text{-}C_3H_7NH_2)W(CO)_5$	Sealed tube	120°/7h	Yellow crystals 82	61.7	25.0 (25.0)	2.1 (2.3)	3.6 (3.7)
$(i\text{-}C_3H_7NH_2)_2W(CO)_4$	Sealed tube	145°/10h	Yellow solid 140(dec.)	60.4	28.8 (29.0)	4.3 (4.3)	6.7 (6.7)
$(i\text{-}C_3H_7)_2NHW(CO)_5$	UV		Yellow solid 130	58.3	31.1 (31.1)	3.3 (3.5)	3.2 (3.3)
$(C_4H_9NH_2)W(CO)_5$	Sealed tube	115°/10h	Yellow 66	69.3	27.3 (27.2)	2.9 (2.7)	3.4 (3.5)
$(C_4H_9NH_2)_2W(CO)_4$	Reflux	6h	Yellow solid 125 (dec.)	45.4	32.2 (32.5)	4.0 (5.0)	6.3 (6.3)
$(C_6H_{11}NH_2)W(CO)_5$	Sealed tube	110°/6h	Needle-shaped yellow crystals 125 (dec.)	60.2	30.6 (31.1)	3.4 (3.0)	3.3 (3.3)
$(C_6H_{11}NH_2)_2W(CO)_4$	Reflux	20h	Light-yellow crystals 200 (dec.)	68.2	38.9 (38.8)	5.4 (5.3)	5.4 (5.6)
$(C_3H_5NH_2)W(CO)_5$	Sealed tube	120°/4h	Yellow crystals 72	68.9	24.9 (25.1)	1.7 (1.8)	3.6 (3.6)
$(C_5H_{11}N)W(CO)_5$	Sealed tube	110°/6h	Yellow crystals 103	84.9	29.1 (29.3)	2.5 (2.6)	3.3 (3.4)
$(C_5H_{11}N)_2W(CO)_4$	Reflux	14h	Deep yellow 198 (dec.)	68.3	36.2 (36.0)	4.8 (4.7)	5.9 (6.0)
$(C_4H_9NO)W(CO)_5$	Sealed tube	125°/6h	Yellow 141(dec.)	71.8	26.2 (26.2)	2.0 (2.1)	3.2 (3.4)
$(C_4H_9NO)_2W(CO)_4$	Reflux	6h	Red yellow 170(dec.)	49.0	30.4 (30.60)	3.7 (3.8)	5.8 (5.9)
$(C_4H_{10}N_2)W(CO)_5$	Sealed tube	80°/8h	Yellow solid 146(dec.)	61.1	26.3 (26.4)	2.5 (2.4)	6.6 (6.8)
$(C_4H_{10}N_2)W(CO)_4$	Reflux	5h	Yellow solid 270 (dec.)	66.9	24.9 (25.1)	2.5 (2.6)	7.3 (7.3)
$(o\text{-}CH_3C_5H_4N)W(CO)_5$	Sealed tube	110°/10h	Yellow crystals 110	52.3	31.3 (31.7)	1.5 (1.6)	3.3 (3.3)
$(C_9H_7N)W(CO)_5$	Sealed tube	180°/10h	Yellow crystals 152(dec.)	83.4	36.8 (37.1)	1.6 (1.5)	3.1 (3.0)
$(C_6H_5CH_2NH_2)W(CO)_5$	Sealed tube	115°/9h	Yellow solid 120	63.9	33.3 (33.4)	2.2 (2.1)	3.0 (3.2)
$(C_6H_5CH_2NH_2)_2W(CO)_4$	Reflux	5h	Yellow solid 192 (dec.)	57.0	42.2 (42.3)	3.3 (3.5)	5.6 (5.4)

trans C—O group 2.4 times as much as the *cis* CO groups in monosubstituted derivatives, and 1.7 to 2.1 times as much as in the disubstituted derivatives.

Experimental

General

Tungsten hexacarbonyl (Diamond Alkali Corporation, U.S.A.) was sublimed before use. Isopropylamine was used as 70% aqueous solution but the other amines were used neat. Reactions and manipulations were carried out under dry nitrogen or in vacuo. Unreacted tungsten hexacarbonyl was removed by sublimation from the reaction product at 50°/1 mm. A quartz vessel fitted with accessories for gas measurement and with an ultraviolet lamp (Philips, 30 W) was used for UV irradiation under nitrogen. IR spectra were measured on a Perkin—Elmer 521.

Substitution reactions

Ethylaminetungsten pentacarbonyl. Tungsten hexacarbonyl (0.2 g) and ethylamine (0.8 ml of 50 % aqueous solution) were heated in an evacuated sealed tube at 80° for 8 h. The product was removed from the tube using a little petroleum ether (40°-60°) and the solvent was evaporated in vacuo. Unreacted tungsten hexacarbonyl was removed by sublimation to leave a bright yellow residue of ethylaminetungsten pentacarbonyl (0.156 g, 74.6%), m.p. 85°. (Found: C, 22.4; H, 2.0; N, 3.4. $C_7H_7NO_3W$ calcd.: C, 22.7; H, 1.9; N, 3.7%).

The compound, which is soluble in most organic solvents, has also been prepared by a UV irradiation in ca. 5% yield.

Preparation and characterization data of other mono- and di-substituted compounds are given in Table 6.

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