

Sulphur Ligand Metal Complexes. Part 10 [1]. Sulphur–Nitrogen Donor Ligand Complexes of the Group 6 Metal Carbonyls

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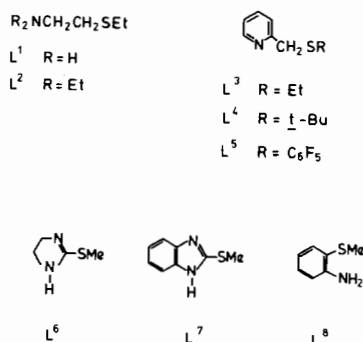
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The interaction of the following sulphur-nitrogen ligands with the group 6 metal carbonyls has been studied: 2-ethylthioethylamine (L^1), *N,N*-diethyl-2-ethylthioethylamine (L^2), 2-(2-thiabutyl)pyridine (L^3), 2-(3,3-dimethyl-2-thiabutyl)pyridine (L^4), 2-(2-pentafluorophenyl-2-thiaethyl)pyridine (L^5), 2-methylthio-2-imidazoline (L^6), 2-methylthio-2-imidazole (L^7) and 2-methylthioaniline (L^8). Bridged ligand complexes $[M(CO)_5]_2(\mu-L^1)$ ($M = Cr$ or W), chelated ligand complexes $M(CO)_4L$ ($M = Cr, Mo$ or $W, L = L^1, L^2, L^3$ or $L^4; M = W, L = L^5$), and unidentate ligand complexes $M(CO)_5L$ ($M = Cr, Mo$ or $W, L = L^6; M = Cr$ or $W, L = L^7$ or L^8) have been isolated and characterized by various spectroscopic techniques. The L^6 and L^7 ligands bind to the metal via the $-N=$ nitrogen whereas the L^8 ligand binds via the thioether sulphur.

Introduction

None of the previous investigations into Group 6 metal carbonyl complexes of mixed sulphur–nitrogen donors [2, 3] have involved the use of potential chelating ligands. In this paper, therefore, we report the results of a study into the interaction of such ligands with the carbonyls of chromium, molybdenum and tungsten. The ligands used all contain a thioether type sulphur and the nitrogen is either an aliphatic amine (L^1, L^2 and L^8), or is involved in an unsaturated ring system (L^3-L^7).

Various complex types have been isolated and characterized. For L^1 , both bridged ligand $[M(CO)_5]_2(\mu-L^1)$ ($M = Cr$ or W) and chelated ligand $M(CO)_4L^1$ ($M = Cr, Mo$, or W) complexes have been obtained, but for L^2-L^5 , only chelate complexes were isolated, viz. $M(CO)_4L$ ($M = Cr, Mo$, or W ,



$L = L^2-L^4; M = W, L = L^5$). In contrast, the ligands L^6-L^8 act in a monodentate fashion, affording the pentacarbonyl complexes $M(CO)_5L$ ($M = Cr, Mo$, or $W, L = L^6; M = Cr$ or $W, L = L^7$ or L^8), with the ligand attachment via a nitrogen atom in the case of L^6 and L^7 , and via the sulphur donor for L^8 .

Experimental

I.r. spectra were recorded on a Beckman I.R. 20 spectrophotometer, 1H n.m.r. spectra on a JEOL JNM-C-60 HL spectrometer and ^{13}C n.m.r. on a JEOL FX60 fourier transform spectrometer. Electronic spectra were obtained using a Shimadzu MPS-5000 instrument and mass spectra on an A.E.I. M.S. 9 spectrometer at 70 eV. Microanalyses (Table I) were carried out by Professor A. D. Campbell (University of Otago).

All solvents were dried according to established procedures. Reactions were carried out under oxygen-free dinitrogen and all complexes were routinely dried *in vacuo*.

The ligands

2-ethylthioethylamine (L^1) and 2-methylthio-2-imidazoline (L^6) were purchased as their hydrochloride (L^1) and hydroiodide (L^6) salts from B.D.H. Chemicals Ltd. and Aldrich Chemical Co. respec-

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TABLE I. Analytical Data and Melting Points of the Complexes.

Complex	Analyses ^a /%				M.p. ^b /°C
	C	H	N	S	
[Cr(CO) ₅] ₂ (μ-L ¹)	34.3(34.4)	2.95(2.3)		6.1(6.55)	72–5
[W(CO) ₅] ₂ (μ-L ²)	22.55(22.3)	1.65(1.5)		5.0(4.3)	83–4
Cr(CO) ₄ L ¹	35.8(35.7)	4.1(4.1)		12.4(11.9)	114–7
Mo(CO) ₄ L ¹	30.5(30.7)	3.6(3.5)		10.2(10.2)	117–8
W(CO) ₄ L ¹	23.2(23.95)	2.9(2.8)		8.5(8.0)	150–1
Cr(CO) ₄ L ²	42.45(44.3)	5.9(5.9)	4.0(4.3)		^c
Mo(CO) ₄ L ²	39.55(39.0)	5.25(5.2)	3.95(3.8)	8.5(8.7)	^c
W(CO) ₄ L ²	31.7(31.5)	4.3(4.2)	3.2(3.1)	7.4(7.0)	92–4
Cr(CO) ₄ L ³	45.4(45.4)	3.55(3.5)	4.75(4.4)	9.6(10.1)	110–11
Mo(CO) ₄ L ³	39.7(39.9)	3.0(3.1)	3.85(3.9)	9.1(8.9)	130–2
W(CO) ₄ L ³	32.7(32.1)	2.9(2.5)	3.1(3.1)	7.3(7.1)	161–3
Cr(CO) ₄ L ⁴	49.0(48.7)	4.7(4.4)	4.0(4.1)		125–7
Mo(CO) ₄ L ⁴	43.6(43.2)	3.9(3.9)	2.6(3.6)		134–6
W(CO) ₄ L ⁴	35.6(35.2)	3.3(3.2)	2.9(2.9)		169–70
W(CO) ₄ L ⁵	32.0(32.7)	1.4(1.0)	1.8(2.4)		100 dec
Cr(CO) ₅ L ⁶	35.4(35.1)	2.7(2.6)	9.1(9.1)		100 dec
Mo(CO) ₅ L ⁶	30.8(30.7)	2.4(2.3)	8.9(8.0)		125 dec
W(CO) ₅ L ⁶	24.8(24.7)	2.2(1.8)	6.8(6.4)		167 dec
Cr(CO) ₅ L ⁷ ^d	46.6(46.6)	3.2(2.8)	9.2(9.6)		> 230
W(CO) ₅ L ⁷	32.0(32.0)	1.6(1.65)	5.7(5.7)		167–9
Cr(CO) ₅ L ⁸ ^e	48.9(48.1)	4.0(4.3)	3.7(3.7)		oil
W(CO) ₅ L ⁸ ^f	33.15(33.45)	2.75(2.6)			70–2

^aCalculated values given in parenthesis. ^bdec = decomposed. ^cNot recorded. ^dContains 0.5 mol L⁷ of solvation. ^eContains 0.5 mol n-hexane. ^fContains 0.25 mol n-hexane.

tively. Neutralization of the salts with aqueous 2 M NaOH followed by diethylether extraction yielded the free ligands. N,N-diethyl-2-ethylthioethylamine (L²) was prepared from 2-diethylaminoethanethiol hydrochloride (Aldrich Chemical Co.), sodium ethoxide and iodomethane, following a method similar to that described for 2-ethylthioethylamine [4].

2-(2-thiabutyl)pyridine (L³), 2-(3,3-dimethyl-2-thiabutyl)pyridine (L⁴) and 2-(2-pentafluorophenyl-2-thiaethyl)pyridine (L⁵) were prepared from 2-picolychloride hydrochloride (Aldrich Chemical Co.), sodium ethoxide and the appropriate thiol (Aldrich Chemical Co.) following a modification of the literature method for 2-(2-thiapropyl)pyridine [5]. The ligands L¹–L⁵ were all freshly distilled under reduced pressure before use, L⁶ was recrystallized from diethylether, and 2-methylthiobenzimidazole (L⁷) and 2-methylthioaniline (L⁸) were used as purchased (Aldrich Chemical Co.).

The Complexes [M(CO)₅]₂(μ-L¹) (M = Cr or W)

These were obtained by similar methods of which the following is typical.

The complex W(CO)₆ (0.704 g, 2 mmol) was dissolved in 60 cm³ tetrahydrofuran (thf) and the solution irradiated in a u.v. cell for 1 hr [1]. The ligand L¹ (0.105 g, 1 mmol), dissolved in thf (20 cm³), was added to the orange solution and the mixture stirred for 10 min, before filtering through Kieselguhr. The solvent was completely removed under vacuum and the excess of W(CO)₆ sublimed from the residue *in vacuo* at room temperature. After the residue was extracted into benzene, cyclohexane was added and the solution cooled to 4 °C. The resulting yellow crystals were washed with cyclohexane. Yield 0.312 g (50%).

The Complexes M(CO)₄L (M = Cr, Mo or W, L = L²–L⁴; M = W, L = L⁵)

These were obtained by similar methods of which the following is typical.

After the complex Cr(CO)₆ (0.660 g, 3 mmol) in thf was irradiated for 1 hr, the ligand L¹ (0.316 g, 3 mmol) was added and the irradiation continued for a further 1½ hr. After filtering through Kieselguhr, the thf was removed under vacuum and the unreacted Cr(CO)₆ sublimed *in vacuo* from the

TABLE II. I.r. and ¹H N.m.r. Spectral Data for the Complexes.

Compound	$\nu(\text{CO})^a/\text{cm}^{-1}$	Solvent	Chemical Shift, $\delta^e/\text{p.p.m.}$
L ¹			
[Cr(CO) ₅] ₂ ($\mu\text{-L}^1$)	2071 w, 1987 w, 1948 sh, 1940s, 1926 m	b	1.25t (CH ₃), 2.55m (CH ₂), 4.66s (NH ₂)
[W(CO) ₅] ₂ ($\mu\text{-L}^1$)	2076 w, 1988 m, 1945s, 1933s, 1927 sh	b	1.41t (CH ₃), 2.71m (CH ₂)
Cr(CO) ₄ L ¹	2017 w, 1905 m, 1889s, 1870 m	b	f
Mo(CO) ₄ L ¹	2019 m, 1901s, 1883 sh, 1845s	c	f
W(CO) ₄ L ¹	2018 m, 1894s, 1881s, 1843s	c	f
L ²			
Cr(CO) ₄ L ²	2013 w, 1898s, 1880s, 1840 m	c	1.17m (CH ₃), 2.61m (CH ₂)
Mo(CO) ₄ L ²	2022 w, 1903s, 1884s, 1842 m	c	1.31m (CH ₃), 2.85m (CH ₂)
W(CO) ₄ L ²	2015 w, 1894 sh, 1882s, 1840s	c	1.31m (CH ₃), 2.95m (CH ₂)
L ³			
Cr(CO) ₄ L ³	2016 w, 1909s, 1892s, 1852 m	c	1.25t (CH ₃), 2.55q (CH ₂ CH ₃), 3.90s (pyCH ₂ S), 7.40m (py), 8.64m ($\alpha\text{-H}$)g
Mo(CO) ₄ L ³	2023 w, 1915s, 1898s, 1853 m	c	1.35t (CH ₃), 2.50q (CH ₂ CH ₃), 4.02s (pyCH ₂ S), 7.35m (py), 9.03m ($\alpha\text{-H}$)
W(CO) ₄ L ³	2017 w, 1897s, 1886s, 1844 m	c	1.34t (CH ₃), 2.59q (CH ₂ CH ₃), 4.10s (pyCH ₂ S), 7.40m (py), 8.99m ($\alpha\text{-H}$)
L ⁴			
Cr(CO) ₄ L ⁴	2014 m, 1909 m, 1896s, 1871 m	b	1.33t (CH ₃), 2.69q (CH ₂ CH ₃), 4.27s (pyCH ₂ S), 7.40m (py), 9.13m ($\alpha\text{-H}$)
Mo(CO) ₄ L ⁴	2020 w, 1906s, 1913 m, 1876 m	b	1.36s (CH ₃), 3.94s (pyCH ₂ S), 7.35m (py), 8.55m ($\alpha\text{-H}$)
W(CO) ₄ L ⁴	2015 w, 1905 m, 1894s, 1874 m	b	1.30s (CH ₃), 4.08s (pyCH ₂ S), 7.40m (py), 9.01m ($\alpha\text{-H}$)
L ⁵			
Cr(CO) ₅ L ⁵	2020 w, 1914s, 1895 sh, 1856 m	c	1.33s (CH ₃), 4.12s (pyCH ₂ S), 7.45m (py), 9.87m ($\alpha\text{-H}$)
L ⁶			
Cr(CO) ₅ L ⁶	2069 m, 1934s, 1889 m	d	f
Mo(CO) ₅ L ⁶	2070 w, 1937 sh, 1932s, 1888 m	d	2.49s (CH ₃), 3.67s (CH ₂), 4.02s (NH)
W(CO) ₅ L ⁶	2066 m, 1924s, 1920 sh, 1880 m	d	2.44s (CH ₃), 3.66m (CH ₂), 4.78s (NH)
L ⁷			
Cr(CO) ₅ L ⁷	2069 w, 1938s, 1927s, 1883s	d	2.44s (CH ₃), 3.71m (CH ₂), 4.84s (NH)
W(CO) ₅ L ⁷	2074 w, 1932 sh, 1927s, 1888 m	d	f
L ⁸			
Cr(CO) ₅ L ⁸	2071 m, 1984 w, 1945s, 1933s	b	2.72s (CH ₃), 3.00s (NH), 7.20m (Ar) ^b
Mo(CO) ₅ L ⁸	2080 w, 1987 m, 1951s, 1934 sh	b	2.87s (CH ₃), 5.00s (NH), 7.25m and 7.90m (Ar) ^b
W(CO) ₅ L ⁸	2076 m, 1983 m, 1945 sh, 1941s, 1931 sh	b	2.91s (CH ₃), 3.44s (NH), 7.25m and 7.80m (Ar) ^b
			2.33s (CH ₃), 4.21s (NH ₂), 7.00m (Ar)
			2.65s (CH ₃), 4.20s (NH ₂), 7.10m (Ar)
			f
			2.89s (CH ₃), 3.70s (NH ₂), 7.10m (Ar)

^aw = weak, m = medium, s = strong, sh = shoulder.^bCyclohexane.^cCHCl₃.^dNitromethane.^eIn CDCl₃ unless otherwise stated.^fNot recorded or decomposed in CDCl₃.^g $\alpha\text{-H}$ = proton α to pyridine nitrogen.^hIn (CD₃)₂CO.ⁱs = singlet, t = triplet, q = quartet, m = multiplet.

TABLE III. ^{13}C N.m.r. Spectral Data for $\text{M}(\text{CO})_4\text{L}^1$ Complexes.

Complex	Chemical Shift, δ^a /p.p.m.		
	<i>cis</i> -CO	<i>trans</i> -CO (to S)	<i>trans</i> -CO (to N)
$\text{Cr}(\text{CO})_4\text{L}^1$	216.1	226.5	227.9
$\text{Mo}(\text{CO})_4\text{L}^1$	207.0	219.1	219.5

^aIn C_6D_6 .

residue. The resultant solid was dissolved in benzene to give a yellow solution which was reduced in volume and then cyclohexane added to induce crystallization. The resulting yellow precipitate was washed with cyclohexane. Yield 0.510 g (63%). In the case of $\text{M} = \text{Cr}$ or W and $\text{L} = \text{L}^2$, purification was achieved by silica-gel (100–200 mesh) chromatography, eluting with benzene.

The Complexes $\text{M}(\text{CO})_5\text{L}$ ($\text{M} = \text{Cr}, \text{Mo},$ or $\text{W}, \text{L} = \text{L}^6$; $\text{M} = \text{Cr}$ or $\text{W}, \text{L} = \text{L}^7$ or L^8)

These were obtained by similar methods of which the following is typical.

After irradiating the complex $\text{Cr}(\text{CO})_6$ (0.660 g, 3 mmol) in thf, the ligand L^6 (0.349 g, 3 mmol) was added and the solution stirred for 5 min. The residue, obtained from the thf solution, as in the above method, was extracted into benzene, concentrated, and n-pentane added. The product, which was obtained as a yellow precipitate, was washed with n-pentane. Yield 0.656 g (75%).

In the case of $\text{M} = \text{W}$ and $\text{L} = \text{L}^6$, purification was achieved by chromatography on silica-gel (100–200 mesh) using acetone as eluent. For the L^7 ligand complexes the thf residue was extracted with benzene, then acetone, the product being obtained from the latter extraction, and for the L^8 ligand complexes n-hexane was used. Attempts to convert the $\text{M}(\text{CO})_5\text{L}$ complexes into chelated ligand complexes, by further irradiation, were unsuccessful. The complexes $\text{M}(\text{CO})_5(\text{bi})$ ($\text{M} = \text{Cr}$ or W , bi = benzimidazole) were prepared according to a literature method [3].

Results and Discussion

The Complexes $[\text{M}(\text{CO})_5]_2(\mu\text{-L}^1)$ ($\text{M} = \text{Cr}$ or W)

These were obtained as moderately air-stable crystalline, yellow solids on addition of L^1 (1 mol) to u.v.-irradiated tetrahydrofuran solutions of the appropriate metal carbonyl complex (2 mol). Attempts to prepare bridged ligand complexes with the ligands $\text{L}^2\text{--L}^5$ were unsuccessful, although pentacarbonyl species were detected in reaction mixtures by i.r. spectroscopy. On work up (e.g. by silica gel chromatography) such species decomposed

or were converted to the chelated ligand, $\text{M}(\text{CO})_4\text{L}$, complexes discussed below. In fact the isolated bridged ligand L^1 complexes can also be readily decomposed in solution, (e.g. $[\text{W}(\text{CO})_5]_2(\mu\text{-L}^1)$ after 5 min refluxing in cyclohexane, is completely converted to $\text{W}(\text{CO})_4\text{L}^1$ and $\text{W}(\text{CO})_6$). Space filling molecular models show steric interactions between the bridging ligand and the $\text{M}(\text{CO})_5$ unit are increased considerably if the nitrogen donor atom is changed from a primary amine (as in L^1) to a tertiary amine (as in L^2) or a 2-substituted pyridine ($\text{L}^3\text{--L}^5$). I.r. data show a carbonyl-stretching frequency pattern (Table II) consistent with $\text{M}(\text{CO})_5\text{L}$ systems [6] with the $\nu(\text{CO})$ values lying below those found for bridged ligand complexes of dithioether ligands [7]. The observations that the $\nu(\text{NH})$ frequencies are similar to those observed [7] for the complexes $[\text{M}(\text{CO})_5]_2(\mu\text{-en})$ ($\text{M} = \text{Cr}$ or W , en = ethylenediamine) and that both the methylene and methyl proton resonances shift downfield in the n.m.r. (Table II) on coordination are consistent with the bridging nature of the ligand.

The Complexes $\text{M}(\text{CO})_4\text{L}$ ($\text{M} = \text{Cr}, \text{Mo}$ or $\text{W}, \text{L} = \text{L}^1\text{--L}^4$; $\text{M} = \text{W}, \text{L} = \text{L}^5$)

The chelated ligand $\text{M}(\text{CO})_4\text{L}$ complexes were most conveniently prepared by the photochemical method (see Experimental Section). I.r. and ^1H n.m.r. spectral data for the complexes are listed in Table II. In the i.r., the observed $\nu(\text{CO})$ frequencies are characteristic of $\text{M}(\text{CO})_4\text{L}$ ($\text{L} =$ chelating ligand systems [6]. For the ligand L^5 , the influence of the electron withdrawing pentafluorophenyl group attached to the sulphur donor atom is readily apparent. A comparison of the $\nu(\text{CO})$ data, obtained in CHCl_3 , for the series $\text{W}(\text{CO})_4\text{L}$ ($\text{L} = \text{L}^1\text{--L}^3$ and L^5) shows the frequencies to lie at higher wavenumbers for the L^5 ligand complex, in line with a reduced electron availability at the metal centre. In the ^1H n.m.r. spectra of the L^3 and L^4 ligands, the proton α to the pyridyl nitrogen can be distinguished from the multiplet signal of the other aromatic protons as a resonance which moves downfield by about 0.4 p.p.m. in the complexes. ^{13}C n.m.r. data have been obtained for the complexes $\text{M}(\text{CO})_4\text{L}^1$ ($\text{M} = \text{Cr}$ and Mo) (Table III). The outstanding feature

TABLE IV. Force Constant Data and Low Energy Absorption Maxima for $M(\text{CO})_5\text{L}$ Complexes.

Complex ^a	CO Force Constants ^b /N m ⁻¹		λ_{max} ^c /nm
	k ₁	k ₂	
Cr(CO) ₅ L ⁶	1458	1578	407 (3.46)
Cr(CO) ₅ L ⁷	1455	1575	406 (3.50)
Cr(CO) ₅ (bi)	1443	1584	405 (3.42)
[Cr(CO) ₅] ₂ (μ -en) ^d	1451	1587	410 (3.77)
Cr(CO) ₅ L ⁸	1528	1590 ^g	437
[Cr(CO) ₅] ₂ (μ -bmtt) ^e	1529	1598 ^g	445 (3.22)
W(CO) ₅ L ⁶	1446	1564	398 (3.52), 432sh (3.02)
W(CO) ₅ L ⁷	1459	1575	392 (3.50), 423sh (2.92)
W(CO) ₅ (bi)	1444	1567	395 (3.45), 426sh (2.90)
[W(CO) ₅] ₂ (μ -bmtt) ^e	1499	1592	395sh (3.62), 417 (3.64), 442sh (2.98)
W(CO) ₅ L ⁸	1526	1589 ^g	392, 440sh
[W(CO) ₅] ₂ (μ -bett) ^e	1533	1594 ^g	382 (3.51), 411sh (3.43), 443sh (2.63)

^aLigand abbreviations: bi = benzimidazole, en = ethylenediamine, bmtt = 3,4-bis(methylthio)toluene, bett = 3,4-bis(ethylthio)toluene. ^bCalculated from CO stretching frequencies (recorded in nitromethane) according to ref. 14. ^cObtained in EtOH, log ϵ in parenthesis. ^dFrom ref. 7. ^eFrom ref. 1. ^fIn cyclohexane.

of these spectra is the appearance of two ¹³C resonances corresponding to the carbonyls *trans* to the L¹ ligand and assignments can be made following the expectation that a CO *trans* to an amine [8] will show a greater downfield shift than a CO *trans* to a sulphide [1].

The Complexes $M(\text{CO})_5\text{L}$ ($M = \text{Cr}, \text{Mo}$ or W , $L = \text{L}^6$; $M = \text{Cr}$ or W , $L = \text{L}^7$)

These complexes were isolated in a manner similar to that described for the $[\text{M}(\text{CO})_5]_2(\mu\text{-L}^1)$ complexes. Evidence for the unidentate nature of the ligands, binding through a nitrogen donor atom comes from spectral data: i.r. spectra, obtained in nitromethane solutions, in the 1800–2100 cm⁻¹ range (Table II) show a carbonyl-stretching frequency pattern typical of $\text{M}(\text{CO})_5\text{L}$ complexes where L is a unidentate nitrogen donor ligand, the frequencies not being as high as expected for corresponding complexes of sulphides [1, 7]. Moreover, calculated Cotton–Kraihanzel force constants (Table IV) are similar to values obtained for the complexes $\text{M}(\text{CO})_5(\text{bi})$ (bi = benzimidazole) and $[\text{M}(\text{CO})_5]_2(\mu\text{-en})$ (en = ethylenediamine). Nitrogen–hydrogen stretching frequency data, recorded in CHCl₃, for the complexes are as follows: L = L⁶, M = Cr 3452, M = Mo 3460, M = W 3474 (free L⁶ 3431 cm⁻¹); L = L⁷, M = Cr 3467, M = W 3482 (free L⁷ 3460 cm⁻¹). That the $\nu(\text{NH})$ frequency moves to higher energy relative to the free ligands is taken as evidence for the coordination of the –N= nitrogen rather than the NH nitrogen. Downfield shifts of the NH resonance on coordination (>0.4 p.p.m.) are greater

than those observed for the –SCH₃ resonance (<0.2 p.p.m.) (Table II). Sulphur coordination would be expected to induce a greater deshielding of the methyl protons as for the L⁸ ligand complexes discussed below. In the free ligand, L⁶, the –(CH₂)₂–methylene protons are observed as only one resonance, but on complexation a multiplet is observed, showing the protons have become inequivalent through nitrogen coordination. Similarly, the free ligand, L⁷, shows a symmetrical, but complex multiplet, for the aromatic protons. However this becomes asymmetrical in the complexes, and one aryl proton can be clearly distinguished downfield from the others. A similar asymmetry is also observed for the complexes, $\text{M}(\text{CO})_5(\text{bi})$ [9]. The electronic spectral curves, in the range 350–450 nm, for the L⁶ and L⁷ ligand complexes, are virtually identical to those recorded for the analogous $\text{M}(\text{CO})_5(\text{bi})$ complexes (Table IV), where the ligand must bind via the nitrogen. The band which occurs in this region has been assigned to a ¹A₁ → ¹E type transition and the low energy shoulder for the W complexes to a ¹A₁ → ³E transition [10]. The wavelength of the ¹A₁ → ¹E band is sensitive to the nature of the donor atom in the complex [7, 10], but since $\text{M}(\text{CO})_5\text{L}$ complexes containing ligands with –SR groups attached to aromatic residues also can give rise to bands of similar energy [1], such evidence must be treated with caution.

The Complexes $\text{M}(\text{CO})_5\text{L}^8$ ($M = \text{Cr}, \text{Mo}$ or W)

The 2-methylthioaniline complexes are thermally unstable and were only isolated with difficulty.

The Mo complex could not be obtained analytically pure however the mass spectrum of the oil showed a parent molecular ion corresponding to $[\text{Mo}(\text{CO})_5\text{L}^8]^+$ followed by the expected CO loss, as for the analogous Cr and W complexes. Gentle refluxing in the presence of excess triphenylphosphite affords complete ligand substitution (e.g. i.r. spectroscopy shows $\text{W}(\text{CO})_5\text{L}^8$ is converted to $\text{W}(\text{CO})_5\text{P}(\text{OPh})_3$ within 10 min). Evidence that the complexes contain the ligand bound in a unidentate fashion through the sulphur is as follows: carbonyl stretching frequency (Table II) and Cotton–Kraihanzel force constant data (Table IV) fall in the range expected for $\text{M}(\text{CO})_5\text{L}$ (L = thioether ligand) complexes and above the range for N donor ligands [1]. The $\nu(\text{NH})$ bands shift to increased wave numbers on coordination of the L^8 ligand. The $\nu(\text{NH})$ data, recorded in CHCl_3 , are as follows: M = Cr 3472, 3387, M = W 3466, 3360, (free L^8 3461, 3364 cm^{-1}). Shifts of 95–130 cm^{-1} to lower wave numbers have been observed previously for $\nu(\text{NH})$ in a series of $\text{W}(\text{CO})_5$ -(amine) complexes where the amine nitrogen is definitely coordinated [11]. In the n.m.r. (Table II) the NH proton resonance does not move down-field, but the $-\text{SCH}_3$ proton resonance does (by over 0.3 p.p.m.) indicating S coordination.

Aniline is a weaker base, due to electron delocalization, than heterocyclic amines such as imidazole [12, 13], and the complexes it forms with zero valent Cr, Mo and W are readily dissociated [12]. The thioether sulphur is therefore the preferred binding site. In the case of the ligands L^6 and L^7 , however, the thioether sulphur lies between two electronegative N atoms, which must reduce its basicity sufficiently to make the soft $-\text{N}=\text{N}$ nitrogen the preferred donor atom. Molecular models indicate there should be no steric constraints to sulphur binding.

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