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MOLYBDENUM AND TUNGSTEN CARBONYL COMPLEXES WITH MACROCYCLIC THIAETHER LIGANDS

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Summary

The macrocyclic tetradentate thiaether ligands 1,4,8,11-tetrathiacyclotetradecane (L^1) and 3,6,10,13-tetrathiabicyclo[13.4.0]nona-1,16,18-triene (L^2) react with $Mo(CO)_6$ and $W(CO)_6$ to give *fac*-$Mo(CO)_3L^1$, *fac*-$Mo(CO)_3L^2$, $[W(CO)_4]_2$-μ-L^1 and *cis*-$W(CO)_4L^2$, respectively. In these compounds the macrocyclic ligands are limited to tridentate (for Mo) or bidentate (for W) ligation. Their ^1H, ^{13}C NMR and infrared spectra are discussed.

Introduction

During studies of molybdenum and tungsten complexes of the potentially tetradentate sulfur-donor ligands 1,4,8,11-tetrathiacyclotetradecane (L^1) and 3,6,10,13-tetrathiabicyclo[13.4.0]nona-1,16,18-triene (L^2) (Fig. 1), we have prepared a series of new tri- and tetra-carbonyl compounds. In a previous study of macrocyclic thiaether

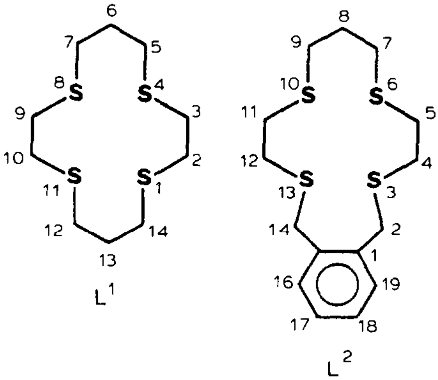


Fig. 1. The ligands L^1 and L^2.

complexes of molybdenum [1] $[Mo_2(CF_3SO_3)_2(H_2O)_4]^{2+}$ was employed to give Mo^{II} and Mo^{IV} complexes with a sixteen-membered macrocyclic sulfur donor. In the present work both the well-known thermal reactions of $Mo(CO)_6$ and photochemical reactions of $W(CO)_6$ are used to obtain zerovalent metal complexes in which the fourteen-membered macrocycles function only as tri- or bi-dentate ligands, respectively.

Experimental

The compounds $Mo(CO)_6$ and $W(CO)_6$ (from Aldrich Chemicals, Milwaukee and Fluka Chemicals, Switzerland, respectively) were used without further purification. The ligands L^1 and L^2 were prepared by the method of Rosen and Busch [2]. All solvents were dried and purified, and reactions were carried out under dry nitrogen unless otherwise indicated.

Decomposition points were measured on a Gallenkamp melting point apparatus and are uncorrected. Conductivity measurements employed a Philips P.R. 9500 direct reading conductivity bridge and sample concentrations of 10^{-3} *M*. Molecular weights were determined by Vapour Pressure Osmometry and electronic spectra were recorded on a Cary 219 spectrophotometer. Infrared spectra were recorded on a Perkin–Elmer 683 infrared spectrophotometer and ^1H and ^{13}C-$\{^1H\}$ NMR spectra were recorded on Varian CFT-20 (79.6 MHz for ^1H, 19.9 MHz for ^{13}C) and Bruker HFX-270 (270 MHz for ^1H, 67.89 MHz for ^{13}C) spectrometers.

Tetrathiaether ligand complexes

fac-Tricarbonyl(1,4,8,11-tetrathiacyclotetradecane)molybdenum(0) (1). A mixture of $Mo(CO)_6$ (0.10 g, 0.38 mmol) and L^1 (0.11 g, 0.40 mmol) in ethanol (10 cm^3) was refluxed for 2.5 h. The light yellow crystals which precipitated were collected by filtration of the hot solution in air, washed with hot ethanol and dried under vacuum. The yield was 0.13 g (80%). Anal. Found: C, 35.1; H, 4.6; N, nil; Mo, 21.3; O, 10.8; S, 28.4. $C_{13}H_{20}MoO_3S_4$ calcd.: C, 34.8; H, 4.5; N, nil; Mo, 21.4; O, 10.7; S, 28.6%. Decomposition point 180°C. Molar conductivity in CH_3NO_2, Λ_0 0.1 Ω^{-1} cm^2 mol^{-1}. Molecular weight in CH_2Cl_2, 451 (calcd. 448). Electronic spectrum in CH_2Cl_2, 332 nm (ε 6680 l cm^{-1} mol^{-1}). The mass spectrum showed peaks characteristic of L^1 only (M^+ $m/z = 268$). The compound is soluble in most organic solvents with the exception of alcohols, ether and n-hexane. Solutions in non-coordinating solvents are stable for a number of days, but in coordinating solvents decomposition occurs.

fac-Tricarbonyl(3,6,10,13-tetrathiabicyclo[13.4.0]nona-1,16,18-triene)molybdenum(0) (2). A mixture of $Mo(CO)_6$ (0.10 g, 0.38 mmol) and L^2 (0.125 g, 0.38 mmol) in ethanol (15 cm^3) was refluxed for 2 h. The light yellow crystals which precipitated were collected by filtration of the hot solution in air, washed with hot ethanol and dried under vacuum. The yield was 0.19 g (80%). Anal. Found: C, 42.4; H, 4.4; N, nil; Mo, 18.9; O, 10.5; S, 24.8. $C_{18}H_{22}MoO_3S_4$ calcd.: C, 42.3; H, 4.3; N, nil, Mo, 18.8; O, 10.2; S, 25.1%. Decomposition point 195°C. The mass spectrum showed peaks characteristic of L^2 only (M^+ $m/z = 330$). The complex is only sparingly soluble in the same solvents as **1** and is also decomposed by coordinating solvents.

μ-1,4,8,11-Tetrathiacyclotetradecanebis[tetracarbonyltungsten(0)] (3). A mixture of $W(CO)_6$ (0.10 g, 0.28 mmol) and L^1 (0.04 g, 0.15 mmol) in ethanol (5 cm^3) was refluxed under constant irradiation from a Wotan XBO 150 W lamp. After 7 h a yellow solid had precipitated. This was filtered off in air and washed with ethanol. The yield was 0.06 g (43%). Anal. Found: C, 25.6; H, 2.8; N, nil; S. 14.7. $C_{18}H_{20}O_8S_4W_2$ calcd.: C, 25.1; H, 2.4; N, nil; S, 14.7%. Decomposition point 200°C. Mass spectrum, as for **1**. The complex is very insoluble in all common organic solvents.

Tetracarbonyl-cis-(3,6,10,13-tetrathiabicyclo[13.4.0]nona-1,16,18-triene tungsten (0) (4). A mixture of $W(CO)_6$ (0.10 g, 0.28 mmol) and L^2 (0.11 g, 0.33 mmol) in ethanol (10 cm^3) was refluxed under constant irradiation from a Wotan XBO 150 W lamp for 4 h. Slow evaporation of the resulting solution (in air) to a volume of ca. 5 cm^3 precipitated a solid which was filtered off. Clusters of yellow crystals were separated by hand and recrystallised from dichloromethane/n-hexane. The yield was 0.044 g (25%). Anal. Found: C, 36.4; H, 3.6; N, nil; O, 10.4; S, 20.5. $C_{19}H_{22}O_4S_4W$ calcd.: C, 36.4; H, 3.5; N, nil; O, 10.2; S, 20.5%. Decomposition point 185°C. Molar conductivity in CH_3NO_2, Λ_0 0.1 Ω^{-1} cm^2 mol^{-1}. Molecular weight in CH_2Cl_2, 650 (calcd. 626). Electronic spectrum in CH_2Cl_2, 372 nm (ε 1990 l cm^{-1} mol^{-1}), 300 nm (ε 10700). Mass spectrum, as for **2**. The complex is similar in solubility to **1** but the ligand is not readily replaced by coordinating solvents.

Results and discussion

The reactions of $M(CO)_6$ (M = Mo, W) with L^1 and L^2 lead to the new air-stable diamagnetic yellow complexes **1**–**4**. The formation of the Mo complexes proceeds smoothly in refluxing ethanol but photolysis of the hot reaction mixture is required for the W complexes. Elemental analysis, conductivity and molecular weight measurements indicate that complexes **1** and **4** are neutral monomeric species in solution. The insoluble complex **2** is assigned a similar structure on the basis of its spectral similarity to **1**. The empirical formula and high insolubility of **3** suggests

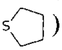
TABLE 1

INFRARED SPECTRA OF THE COMPLEXES[a] (cm^{-1})

Complex	$\nu(CO)$	$\delta(MCO)$	$\nu(M-S)$	$\nu(M-CO)$
1	1925s, 1810sh, 1790s 518s	647s, 615s, 522 sh,	470w	–
1 in CH_2Cl_2	1935s (A_1), 1820s (E) $I_E/I_{A_1} = 2.2$	–	–	–
2	1928s, 1818s, br	647, 615s, 518s	470w	–
2 in CH_2Cl_2	1940s (A_1), 1825s (E) $I_E/I_{A_1} = 2.3$	–	–	–
3	2010s, 1880s, br, 1850sh	610s, 570s, 560sh	465w	385s
4	2010s, 1900sh, 1875s 1840s	610s, 575s	470w	380w
4 in CH_2Cl_2	2020s (A_1), 1895s, 1865s (A_2, B_1, B_2)	–	–	–
4 in benzene	2020 (A_1), 1910s, 1890s, 1878s (A_2, B_1, B_2)	–	–	–

[a] In CsI unless specified; s, strong; br, broad; w, weak; sh, shoulder; I, intensity. Vibration modes are given in parentheses for solution spectra.

that it is the neutral dinuclear complex $[W(CO)_4]_2$-μ-L^1.

Infrared spectra. The major infrared bands of **1**–**4** are presented in Table 1. In dichloromethane solutions compounds **1** and **2** exhibit two intense bands in the ν(CO) region, consistent with a *facial* tricarbonyl configuration [3] (Fig. 2). The bands at 1940 cm^{-1} in both spectra are assigned to the A_1 vibration mode, those at lower frequency being assigned to the E mode (as expected the degenerate mode is roughly twice the intensity of the A_1 mode). The *facial* tricarbonyl configuration of the Mo complexes is preferred since the strongly π-accepting CO ligands can avoid competition for *d*-orbital electron density. Bands of similar energy have been reported for the complexes *fac*-$Mo(CO)_3L$ (L = 3,6,9-trithiaundecane [4]) and *fac*-$Mo(CO)_3L_3$ (L = SMe_2, SEt_2 and ) [5,6].

Complexes of the type *cis*-$M(CO)_4L_2$ and *trans*-$M(CO)_4L_2$ exhibit four and one ν(CO) bands, respectively, the bands of the *cis*-complexes being generally solvent dependent [3]. The presence of four ν(CO) bands in the infrared spectrum of **4** in benzene (Fig. 2) establishes the *cis*-$W(CO)_4L^2$ structure of this complex. The insolubility of **3** has prevented solution spectral study.

The general pattern of ν(CO) bands observed in the solution is also displayed in the solid state. As predicted for *fac*-$M(CO)_3L_3$ complexes the ν(CO) bands of **1** and **2** are Raman active, and are significantly split by solid state interactions. The similar ν(CO) pattern in the spectra of both tungsten complexes supports a *cis*-configuration of the sulphur donor atoms in **3**. The ν(CSC) bands of the free ligands 708, 695 cm^{-1} (for L^1) and 710, 680 cm^{-1} (for L^2) are absent in the spectra of the complexes and this has been taken as evidence of thiaether S-coordination [7,8,9]. Rich spectra

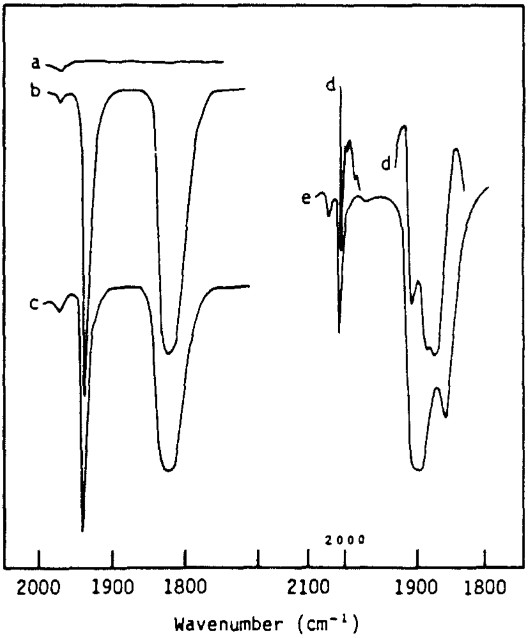


Fig. 2. Solution infrared spectra (a) CH_2Cl_2, (b) **1** in CH_2Cl_2, (c) **2** in CH_2Cl_2, (d) **4** in benzene, (e) **4** in CH_2Cl_2.

associated with ligand vibrations are observed in the 1700–650 cm^{-1} region. Bands due to δ(MCO), ν(M–CO) and ν(M–S) vibrations occur in the 650–250 cm^{-1} region [3]. While a marked difference in the δ(MCO) and ν(M–CO) bands of the Mo and W complexes is anticipated from the disparate CO ligand configurations, the ν(M–S) bands of the complexes are likely to be similar. Consequently the weak bands at ca. 470 cm^{-1}, common to all the spectra, are assigned to ν(M–S). In complexes **1** and **2** bands at 647, 615 and 518 cm^{-1} may be assigned to δ(MoCO) in general agreement with literature values for complexes of the type *fac*-$Mo(CO)_3L_3$ (L = phosphine, δ(MoCO) range 787–468 cm^{-1}) [3]. In the ν(MoCO) region (428–363 cm^{-1}) no strong bands are observed. In complexes **3** and **4** bands at 615, 575 and 565 cm^{-1} may be assigned to δ(WCO). These values compare well with those of *cis*-$W(CO)_4L_2$ (L = phosphine) complexes where less than the six theoretical bands are often observed due to band degeneracy [3]. In contrast to **1** and **2**, a very strong band in the ν(M–CO) region is observed for the tungsten complexes (at ca. 380 cm^{-1}). The identical spectra of the complexes in the 650–250 cm^{-1} region

TABLE 2

^1H AND ^{13}C-{^1H} NMR SPECTRA OF **1** AND **4**

Nucleus, Complex		δ (ppm)	Assignment
^1H,	**1** (25°C)	2.08 pentuplet	CH_2-B
	complex multiplets	CH_2	
	at 2.31, 2.51, 2.79		
	2.93, 3.11, 3.25		
^1H,	**4**	1.7–3.5 m, br, 2.93 s	aliphatic CH_2
	3.81 s, 3.82 s	benzylic CH_2 (next to uncoordinated S)	
	4.25 s, 4.46 s	benzylic CH_2 (next to coordinated S)	
	7.26–7.70 m	CH and CH_2Cl_2	
^{13}C,	**1** (25°C)	25.47, 26.21, 26.51,	CH_2
	30.11, 32.19, 33.95		
	35.34, 38.10, 44.35		
	223.14	CO	
^{13}C,	**1** (−70°C)	24.53, 25.22, 25.89	CH_2
	29.50, 31.50, 31.71,		
	33.95, 34.47, 38.51,		
	43.95		
	223.09	CO	
^{13}C,	**4**	29.94, 32.03, 32.47,	CH_2
	33.64, 34.16, 34.98,		
	35.80, 40.23, 45.54		
	128.50, 129.02,	2° aromatic C	
	129.51, 131.52,		
	134.77, 135.81		
	134.77, 135.81	3° aromatic C	
	204.70	CO	

[a] In CD_2Cl_2 or CH_2Cl_2, relative to Me_4Si: br, broad; m, multiplet; s, singlet. All ^{13}C resonances are singlets. Ligand spectra: L^1 ^1H, δ 1.93 (4H, p, J 6.2 Hz, β-CH_2), overlapping 2.67 (t, J 7.3 Hz), 2.77 (s) total 16 H,α-CH_2 ^{13}C-{^1H}, δ 30.08 (s,α-, β-, propano-), 31.29 (s,α- ethano-): L^2 δ 1.89 (2H, p, J 6.8 Hz, β-CH_2) overlapping 2.71 (t, J 6.6 Hz) and 2.86 (s) total 12 H,α-CH_2, 3.97 (4 H, s, benzylic H), 7.32–7.26 (4H, m aromatics). ^{13}C-{^1H}, δ 30.18 (s, β-CH_2); 30.48, 32.55, 33.20, 33.81 (s, α-CH_2) 127.48, 130.14 (s, aromatic); 136.00 (s, quat. c).

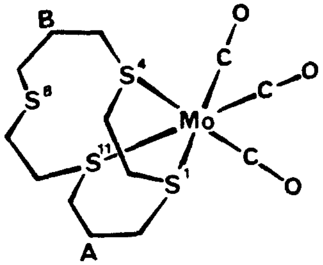


Fig. 3. Proposed structure of **1**.

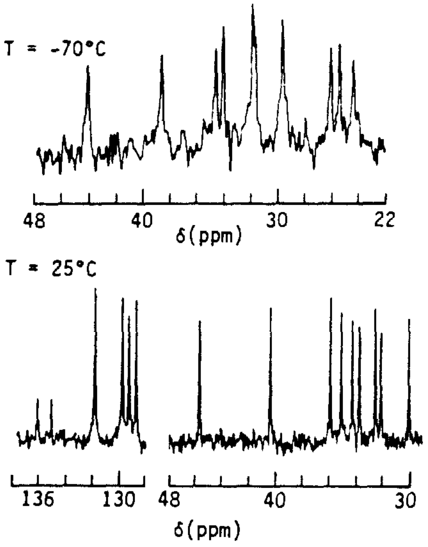


Fig. 4. ^{13}C-$\{^1H\}$ NMR spectra of **1** (top) and **4** (bottom) in CH_2Cl_2 (68 MHz).

further supports similar coordination environments about the molybdenum and tungsten atoms in each class of compound.

NMR spectra. The structural features determined by infrared spectroscopy indicate the tridentate and bidentate coordination of the ligands in the Mo and W complexes, respectively. The ligand conformations of the soluble complexes **1** and **4** have been studied by ^1H and ^{13}C-$\{^1H\}$ NMR spectroscopy. Details of the NMR spectra are given in Table 2. The NMR spectra of **1** are extremely complex in comparison with the simple spectra of free L^1, as a result of the unsymmetrical tridentate coordination of the S_4 ligand. The most prominent resonance in the ^1H NMR spectrum of **1** is a well defined pentuplet at δ 2.08, assigned to a β-propanomethylene group. The resolution and relatively small low field shift of this resonance (cf. L^1 δ 1.93) suggests an essentially free ligand character for this group, identifying it as β-methylene-*B* (Fig. 3). On the other hand the β-CH_2-A resonance would appear at lower field due to the deshielding induced by the binding of S(1) and S(11) and would be split due to the inequivalence of the protons in the locked conformation; these resonances are likely to be present in the δ 2.53 resonance envelope. The complexity of the spectra, not atypical of L^1 complexes [2], prevent further assignments. The ^{13}C-$\{^1H\}$ NMR of **1** (Fig. 4), which is consistent with the unsymmetrical coordination of L^1, exhibits 10 resonances due to the 10 inequivalent CH_2 groups in the S_4-ligand. The presence of only one CO ligand resonance (δ 223.1) indicates fluxionality of the tricarbonyl ligand set. Similar chemical shifts have been reported for other *fac*-$Mo(CO)_3L_3$ (L = phosphine) complexes [10]. Methylene group inequivalence due to the presence of geometrical isomers may therefore be discounted as ligand coordination through any S_3-set produces equivalent structures in the fluxional complex. The unsymmetrical binding of L^1 is consistent with a structure similar

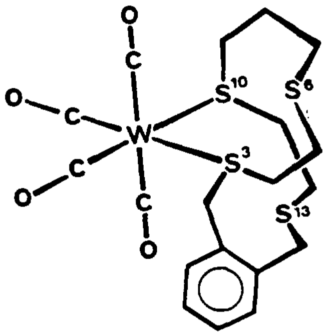


Fig. 5. Proposed structure of **4**.

to that in Fig. 3. An analogous structure is postulated for *fac*-Mo(CO)$_3$L^2 although NMR studies were prevented by its insolubility.

Significant splitting of the single benzylic proton resonance of L^2 (δ 3.97) occurs upon coordination to W(CO)$_4$. The ^{1}H NMR spectrum of **4** exhibits resonances at δ 4.25, 4.46 and 3.81, 3.82 assignable to benzylic protons adjacent to coordinated and uncoordinated sulphur atoms respectively. The benzylic protons adjacent to the coordinated atom resonate at relatively low field due to the deshielding influence of the sulphur atom. Other resonances are due to aliphatic CH$_2$ and aromatic protons. The ^{13}C-{^{1}H} NMR spectrum of **4** (Fig. 4) clearly indicates the unsymmetrical binding of L^2. In the aliphatic CH$_2$ region nine resonances attributable to nine inequivalent carbon atoms are observed. Also, four secondary aromatic and two tertiary aromatic carbon resonances are present, indicating the absence of a symmetry plane bisecting the C(1)–C(15) and C(17)–C(18) bonds of the aromatic ring. The ^{1}H and ^{13}C-{^{1}H} NMR spectra of **4** dictate the binding of L^2 through S(3), S(13) or S(6), S(10) donor atom combinations. The structure proposed for **4** must also account for the inability of the uncoordinated sulphur atoms to bind to another W(CO)$_4$ moiety. Examination of molecular models suggests that S(3), S(10) coordination is that most likely to prevent dimer formation (Fig. 5). The electron withdrawing phenyl group may also contribute to the inability of L^2 to function as a bridging ligand. The unsuitable crystallinity has prevented crystal structure investigation of this interesting conformational aspect. In the metal complexes of L^1 [11], the ligand binding mode appears to be controlled by a combination of factors, including metal ion size (in relation to the macrocyclic cavity), the presence of competing ligands and the electronic nature of the metal ions. The ligand coordination modes observed in the title compounds are dictated not only by the inability of the macrocycles to encircle the metal ions (giving tetradentate ligation), but also by the instability of species formed upon further loss of the stabilizing π-acceptor carbonyl ligand.

Acknowledgements

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