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Seven co-ordinate macrocyclic tetrathioether complexes of molybdenum(II) and tungsten(II)

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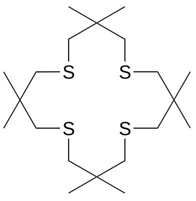
Treatment of $[\{Mo(\mu\text{-}Br)Br(CO)_4\}_2]$ with 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane (Me_8[16]aneS_4) in CH_2Cl_2 gave the crystallographically characterised, seven-co-ordinate, ionic complex $[MoBr(CO)_2(Me_8[16]aneS_4)][MoBr_3(CO)_4]$ **1**. Reaction of 2 equivalents of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with 1 equivalent of Me_8[16]aneS_4 afforded the analogous iodo-complex $[MoI(CO)_2(Me_8[16]aneS_4)][MoI_3(CO)_4]$ **2** and the crystallographically characterised complexes $[WI(CO)_2(Me_8[16]aneS_4)][WI_3(CO)_4]$ **3** and $[WI(CO)_3(Me_8[16]aneS_4)]$-$[WI_3(CO)_4]$ **4**. The cations in complexes **1** and **3** have distorted capped-trigonal-prismatic geometries whereas that in **4** has a geometry lying between capped octahedral and capped trigonal prismatic. The anions of all three complexes have capped-octahedral geometries. Treatment of 2 equivalents of $[MI_2(CO)_3(NCMe)_2]$ with 1 equivalent of 1,5,9,13-tetrathiacyclohexadecane ([16]aneS_4), 1,4,8,11-tetrathiacyclotetradecane ([14]aneS_4) or 1,4,7,10-tetrathiacyclododecane ([12]aneS_4) yielded the bimetallic thioether-bridged complexes $[M_2I_4(CO)_6$-$([n]aneS_4\text{-}S,S',S'',S''')]$ (n = 16, M = Mo; n = 14, M = Mo or W; n = 12, M = Mo), and the ionic complexes $[WI(CO)_2([n]aneS_4)][WI_3(CO)_4]$ (n = 16 or 12). The relationships between the various products of these reactions are discussed. Reaction of [16]aneS_4 with $[MoCl_3(thf)_3]$ (thf = tetrahydrofuran) gave a polymeric complex of empirical formula $[Mo_3Cl_9([16]aneS_4)_2]$ plus the dinuclear, ionic complex $[Mo_2Cl_5([16]aneS_4\text{-}S,S')_2]Cl$.

Macrocyclic tetrathioethers such as Me_8[16]aneS_4, [16]aneS_4, [14]aneS_4 and [12]aneS_4 have become increasingly important in recent years since they can in principle provide low-oxidation-state metal–sulfur sites for model studies of metal-catalysed processes such as nitrogen fixation. To date, however, the only known example of a dinitrogen complex of molybdenum in an all-sulfur co-ligand environment is *trans*-$[Mo(N_2)_2(Me_8[16]aneS_4)]$.[1] With a view to developing new routes to the chemistry of molybdenum complexes of dinitrogen with sulfur co-ligands, we have explored the reactivity of tetrathioether macrocycles with molybdenum(II) and tungsten(II) halogenocarbonyl starting materials. Although a range of complexes of these macrocycles has been reported,[2–14] the only halogenocarbonyl complexes of molybdenum(II) and tungsten(II) to be described to date are $[MI_2(CO)_3([14]aneS_4)]$ (M = Mo or W), prepared by oxidation of $[\{Mo(CO)_3\}_2([14]aneS_4)]$ and $[W(CO)_3([14]aneS_4)]$ with I_2.[15]

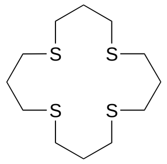
In this paper we describe the reactions of $[\{Mo(\mu\text{-}Br)Br(CO)_4\}_2]$, $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and $[MoCl_3(thf)_3]$ (thf = tetrahydrofuran) with Me_8[16]aneS_4, [16]aneS_4, [14]aneS_4 and [12]aneS_4 to give a variety of complexes. Preliminary results of some of this work have been published.[16,17]

Results and Discussion

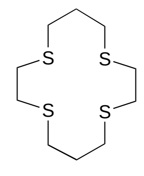
Me_8[16]aneS_4 and [16]aneS_4 complexes



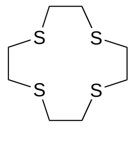
Me_8[16]aneS_4



[16]aneS_4



[14]aneS_4



[12]aneS_4

Reaction of $[\{Mo(\mu\text{-}Br)Br(CO)_4\}_2]$ with an excess of Me_8[16]aneS_4 in CH_2Cl_2 at 20 °C afforded the seven-co-ordinate, ionic complex $[MoBr(CO)_2(Me_8[16]aneS_4)][MoBr_3(CO)_4]$ **1**. Data which characterise this product, and others described here, are in Tables 1 (C, H and S elemental analyses), 2 (IR and ^1H NMR spectroscopy) and 3 (^{13}C NMR and UV/VIS spectroscopy). Conductivity measurements in $MeNO_2$ ($\Lambda_M = 82\ \Omega^{-1}\ cm^2\ mol^{-1}$) confirm that complex **1** is a 1 : 1 electrolyte in solution. The molecular structure of **1**, determined by X-ray diffraction methods, is shown in Fig. 1, and selected bond lengths and angles are given in Table 4. The atom numbering scheme in the thioether macrocycle, common to all the complexes described here, is shown more clearly in Fig. 2. Both the cation and anion contain seven-co-ordinate molybdenum(II), and the way in which the bromide ligands are distributed between cation and anion suggests that the $[\{Mo(\mu\text{-}Br)Br(CO)_4\}_2]$ starting material, which is presumed to be isostructural with its crystallographically characterised tungsten analogue,[18] has in effect undergone heterolytic cleavage during the course of the reaction.

We have, for convenience, described[16] the co-ordination geometry in the cation of complex **1** as a 4 : 3 'piano stool' arrangement, with an S_4 seat and the bromide and two carbonyl groups occupying the positions of the three legs, but the structure is more accurately described as capped trigonal prismatic (see later). The molybdenum atom lies 1.488(2) Å above the mean plane of the four sulfur atoms, which are coplanar to within 0.057(4) Å. The mean distance between adjacent sulfur

Table 1 Colours and analytical data (calculated values in parentheses) for macrocyclic tetrathioether complexes of molybdenum and tungsten

			Analysis (%)		
Complex		Colour	C	H	S
1	$[MoBr(CO)_2(Me_8[16]aneS_4)][MoBr_3(CO)_4]$	Green	27.6 (28.7)	3.9 (3.7)	11.8 (12.1)
2	$[MoI(CO)_2(Me_8[16]aneS_4)][MoI_3(CO)_4]$	Green	24.2 (24.5)	3.3 (3.2)	9.7 (10.0)
3	$[WI(CO)_2(Me_8[16]aneS_4)][WI_3(CO)_4]$	Green	21.8 (21.5)	2.9 (2.8)	8.4 (8.8)
4	$[WI(CO)_3(Me_8[16]aneS_4)][WI_3(CO)_4]$	Orange	22.2 (21.9)	3.0 (2.7)	—
5	$[Mo_2I_4(CO)_6(\mu\text{-}[16]aneS_4\text{-}S,S',S'',S''')]$	Brown	18.2 (18.6)	1.8 (2.1)	10.5 (11.0)
6	$[WI(CO)_2([16]aneS_4)][WI_3(CO)_4]$	Green	16.4 (16.1)	2.1 (1.8)	9.3 (9.6)
7	$[Mo_3Cl_9([16]aneS_4)_2]\cdot 0.5CH_2Cl_2$	Purple	23.7 (23.7)	4.0 (4.0)	20.7 (20.6)
8	$[Mo_2Cl_5([16]aneS_4)_2]Cl\cdot 0.33C_6H_{14}$	Pink	30.7 (30.4)	4.9 (5.2)	25.4 (25.0)
9	$[Mo_2Cl_5([16]aneS_4)_2][BPh_4]\cdot Et_2O$	Pink	47.0 (46.6)	5.5 (5.9)	19.0 (19.1)
10	$[Mo_2I_4(CO)_6(\mu\text{-}[14]aneS_4\text{-}S,S',S'',S''')]$	Rust brown	16.6 (16.9)	2.1 (1.8)	10.9 (11.3)
11	$[W_2I_4(CO)_6(\mu\text{-}[14]aneS_4\text{-}S,S',S'',S''')]$	Orange	15.0 (14.7)	1.6 (1.5)	10.0 (9.8)
12	$[Mo_2I_4(CO)_6(\mu\text{-}[12]aneS_4\text{-}S,S',S'',S''')]$	Rust brown	15.4 (15.2)	1.6 (1.5)	11.9 (11.6)
13	$[WI(CO)_2([12]aneS_4)][WI_3(CO)_4]$	Green	13.4 (13.1)	1.4 (1.3)	9.7 (10.0)

Table 2 Infrared[a] and ^1H NMR data[b] for the macrocyclic tetrathioether complexes of molybdenum(II) and tungsten(II)

complex	$\nu(CO)/cm^{-1}$	^1H NMR, δ, *J*/Hz
1	[c] 2089s, 2023s, 1975 (br), 1947s, 1899s	[d] 3.2–2.4 (br m, 16 H, CH_2), 1.48, 1.41, 1.31, 1.27, 1.26, 1.23 (all s, 24 H, CH_3)
2	[e] 2070s, 2003s, 1964 (br), 1920 (sh), 1884s	[f] 3.1–2.7 (br m, 16 H, CH_2), 1.7–1.5 (m, 24 H, CH_3)
3	[e] 2069s, 2011m, 1988s, 1950s, 1916s, 1865s	[f] 3.0–2.8 (m, 16 H, CH_2), 1.7–1.5 (m, 24 H, CH_3)
4	[e] 2068s, 2036s, 2010 (sh), 1992s, 1967s, 1944m, 1924s	
5	[g] 2069 (br), 1994 (br), 1910 (br)	[h] 2.9 (t, 16 H, CH_2, $J_{HH} = 7.2$), 2.2 (qnt, 8 H, CH_2, $J_{HH} = 7.2$)
6	[g] 2059s, 2000m, 1986s, 1931s, 1912s, 1869s	[i] 3.8–3.6 (br m, 16 H, CH_2), 2.7–2.9 (br m, 8 H, CH_2)
10	[g] 2067 (br), 1977 (br), 1900 (br)	[h] 2.8 (s, 8 H, CH_2), 2.7 (t, 8 H, CH_2, $J_{HH} = 7.2$), 1.85 (qnt, 4 H, CH_2, $J_{HH} = 6.7$)
11	[g] 2026 (br), 1948 (br), 1901 (br)	[h] 2.8 (s, 8 H, CH_2), 2.65 (t, 8 H, CH_2, $J_{HH} = 7.1$), 1.85 (qnt, 4 H, CH_2, $J_{HH} = 6.5$)
12	[g] 2069 (br), 1995 (br), 1913 (br)	[h] 2.9 (br, CH_2)
13	[e] 2067m, 2044m, 2012m, 1964s, 1936s, 1889s	[i] 3.5–3.1 (br m, CH_2)

[a] br = Broad, sh = shoulder, s = strong, m = medium. [b] At 25 °C; s = Singlet, t = triplet, qnt = quintet, m = multiplet, br = broad. [c] Spectrum recorded as CsI disc. [d] Spectrum recorded in CD_2Cl_2. [e] Spectrum recorded in $CHCl_3$ solution between NaCl plates. [f] Spectrum recorded in $CDCl_3$. [g] Spectrum recorded as KBr disc. [h] Spectrum recorded in $(CD_3)_2SO$. [i] Spectrum recorded in CD_3NO_2.

Table 3 Carbon-13 NMR[a] and UV spectroscopic data for selected complexes at 25 °C

Complex	^{13}C NMR, δ, *J*/Hz	λ_{max}[b]/nm
3	[c] 233, 201 (2 s, CO), 48.8–47.8 (m, CH_2), 38.0–34.8 (m, CMe_2, Me)	[d] 630 (200), 410 (1800), 323 (9000), 230 (32 300)
5	[e] 235.9 (s, CO), 41.1, 39.8 (2 s, CH_2)	[d] 639 (255), 441 (7390), 390 (6600), 320 (11 600), 243 (40 800)
11	[f] 231.2 (d, CO, $J_{WC} = 60.9$), 30.1, 29.8, 28.8 (3 s, CH_2)	[g] 390 (2000)
13	[e] 227, 215 (2 s, CO), 39.2, 33.5 (2 br s, CH_2)	[d] 400 (1080), 243 (26 200)

[a] d = Doublet. [b] $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ in parentheses. [c] Spectrum recorded in CD_2Cl_2. [d] Spectrum recorded in MeCN. [e] Spectrum recorded in DCON-$(CD_3)_2$. [f] Spectrum recorded in $(CD_3)_2SO$. [g] Spectrum recorded in dmf.

atoms is 2.99(2) Å. In a projection of the ion onto the S_4 plane the bromide is in a staggered position midway between S(11) and S(12), with the two carbonyl ligands lying more closely under the Mo(1)–S(13) and Mo(1)–S(14) bonds. A second, disordered, bromide ligand (occupancy 5.4%) was located in a similar position with respect to S(12) and S(13), but we did not locate the corresponding carbonyl ligands.

The facial endodentate co-ordination geometry of the tetrathioether macrocycle in complex **1** contrasts with the equatorial endodentate geometries more commonly observed[1,2,7–14] for complexes of $Me_8[16]aneS_4$ and $[16]aneS_4$, in which the metal lies in or close to (< 0.11 Å) the mean plane of the four sulfur atoms. The overall conformation of the macrocycle in **1** is similar to that found in *syn*-equatorial complexes of $Me_8[16]aneS_4$ such as *trans*-$[MoBr_2(Me_8[16]aneS_4)]$.[2] The macrocycles in both structures have approximate 4*mm* symmetry and the torsion angles around the ring follow similar patterns: in **1** the sequence of angles for S–C–C–C, C–C–C–S, C–C–S–C and C–S–C–C is +g, −g, −t, +t, where g and t are *gauche* and *trans* angles with mean (absolute) values of 64.6(7) and 167.1(17)° respectively

Table 4 Selected molecular dimensions in the complexes **1**, **3** and **4**. Bond lengths in Å angles in °. Estimated standard deviations (e.s.d.s) are in parentheses

(*a*) In the cation

	1 M = Mo, X = Br	**3** M = W, X = I	**4** M = W, X = I
M(1)–S(11)	2.624(3)	2.591(3)	2.590(3)
M(1)–S(12)	2.593(3)	2.618(3)	2.549(3)
M(1)–S(13)	2.579(3)	2.545(3)	2.619(3)
M(1)–S(14)	2.546(3)	2.585(3)	
M(1)–X(15)	2.580(2)	2.755(1)	2.806(1)
M(1)–C(16)	1.994(14)	1.945(14)	2.010(16)
M(1)–C(17)	1.951(12)	1.942(15)	1.971(17)
M(1)–C(18)			2.023(16)
M(1)–X(15′)	2.656(24)	2.883(9)	
M(1)–C(16′)		1.81(8)	
S(11)–M(1)–S(12)	71.4(1)	70.6(1)	67.6(1)
S(11)–M(1)–S(13)	107.3(1)	111.5(1)	89.2(1)
S(12)–M(1)–S(13)	70.7(1)	71.2(1)	67.9(1)
S(11)–M(1)–S(14)	71.2(1)	69.8(1)	
S(12)–M(1)–S(14)	112.3(1)	106.2(1)	
S(13)–M(1)–S(14)	69.6(1)	69.4(1)	
S(11)–M(1)–X(15)	86.0(1)	89.1(1)	94.5(1)
S(12)–M(1)–X(15)	89.7(1)	89.4(1)	153.3(1)
S(13)–M(1)–X(15)	150.3(1)	143.7(1)	93.2(1)
S(14)–M(1)–X(15)	139.9(1)	146.8(1)	
S(11)–M(1)–C(16)	168.3(4)	169.0(5)	82.2(5)
S(12)–M(1)–C(16)	103.1(4)	107.8(4)	119.2(4)
S(13)–M(1)–C(16)	79.6(4)	77.4(5)	164.9(5)
S(14)–M(1)–C(16)	120.5(4)	120.5(4)	
X(15)–M(1)–C(16)	83.7(4)	80.0(5)	75.2(4)
S(11)–M(1)–C(17)	111.0(3)	109.3(4)	117.8(5)
S(12)–M(1)–C(17)	167.0(4)	172.9(5)	75.7(4)
S(13)–M(1)–C(17)	119.1(4)	114.7(4)	121.0(5)
S(14)–M(1)–C(17)	80.1(4)	80.1(5)	
X(15)–M(1)–C(17)	77.9(4)	83.5(5)	131.0(4)
C(16)–M(1)–C(17)	72.1(5)	70.8(6)	74.1(7)
S(11)–M(1)–C(18)			167.8(4)
S(12)–M(1)–C(18)			117.0(4)
S(13)–M(1)–C(18)			82.7(4)
X(15)–M(1)–C(18)			77.0(4)
C(16)–M(1)–C(18)			103.6(7)
C(17)–M(1)–C(18)			74.3(6)
S(11)–M(1)–X(15′)	145.6(5)	140.5(2)	
S(12)–M(1)–X(15′)	85.0(5)	87.8(2)	
S(13)–M(1)–X(15′)	86.9(5)	90.9(2)	
S(14)–M(1)–X(15′)	142.6(5)	149.6(2)	
S(11)–M(1)–C(16′)		80.2(20)	
S(12)–M(1)–C(16′)		108.1(20)	
S(13)–M(1)–C(16′)		166.5(20)	
S(14)–M(1)–C(16′)		122.6(21)	
X(15′)–M(1)–C(16′)		75.6(21)	

(*b*) In the anion

	1 M = Mo, X = Br	**3** M = W, X = I	**4** M = W, X = I
M(2)–X(21)	2.655(1)	2.857(1)	2.843(1)
M(2)–X(22)	2.640(2)	2.856(2)	2.873(1)
M(2)–X(23)	2.640(2)	2.851(1)	2.850(1)
M(2)–C(24)	2.025(12)	2.006(18)	2.028(15)
M(2)–C(25)	2.050(11)	1.976(21)	2.019(13)
M(2)–C(26)	2.048(14)	2.029(17)	2.005(15)
M(2)–C(27)	1.959(14)	1.933(21)	1.971(13)
X(21)–M(2)–X(22)	91.4(1)	90.4[a]	90.3[a]
X(21)–M(2)–X(23)	91.2(1)	89.5[a]	86.7[a]
X(22)–M(2)–X(23)	89.7(1)	90.1[a]	90.3[a]
X(21)–M(2)–C(24)	161.9(4)	160.2(6)	159.0(4)
X(22)–M(2)–C(24)	77.6(4)	75.3(6)	75.8(4)
X(23)–M(2)–C(24)	74.6(3)	77.1(6)	77.8(4)
X(21)–M(2)–C(25)	76.8(3)	74.9(5)	79.2(4)
X(22)–M(2)–C(25)	161.4(3)	159.5(5)	164.0(4)
X(23)–M(2)–C(25)	76.4(3)	75.8(5)	77.2(4)
C(24)–M(2)–C(25)	109.7(5)	114.8(8)	110.6(6)
X(21)–M(2)–C(26)	74.2(3)	76.1(5)	75.5(4)
X(22)–M(2)–C(26)	77.1(3)	74.1(6)	78.3(4)
X(23)–M(2)–C(26)	159.8(4)	158.3(6)	158.6(4)
C(24)–M(2)–C(26)	116.3(5)	111.9(8)	115.9(6)
C(25)–M(2)–C(26)	112.6(5)	114.9(8)	110.1(6)
X(21)–M(2)–C(27)	125.0(3)	124.7(6)	127.5(4)
X(22)–M(2)–C(27)	123.2(4)	126.6(7)	121.3(4)
X(23)–M(2)–C(27)	125.9(4)	124.5(7)	128.9(4)
C(24)–M(2)–C(27)	73.0(5)	75.1(9)	73.5(5)
C(25)–M(2)–C(27)	75.4(5)	74.0(9)	74.7(5)
C(26)–M(2)–C(27)	74.3(5)	77.2(9)	72.3(6)

(*c*) Torsion angles in the macrocyclic ligand

	1	**3**	**4**	[b]
S(11)–C(111)–C(112)–C(113)	65.3(10)	64.3(12)	64.6(14)	76.5(5)
C(111)–C(112)–C(113)–S(12)	−67.5(10)	−63.7(12)	−56.4(14)	−79.2(4)
C(112)–C(113)–S(12)–C(121)	−167.0(7)	−171.8(9)	−165.9(10)	179.3(4)
C(113)–S(12)–C(121)–C(122)	159.9(8)	162.3(10)	158.9(11)	−178.0(4)
S(12)–C(121)–C(122)–C(123)	65.8(10)	69.9(13)	63.3(15)	79.0(5)
C(121)–C(122)–C(123)–S(13)	−62.9(11)	−66.9(13)	−66.2(15)	−77.2(5)
C(122)–C(123)–S(13)–C(131)	−171.2(8)	−166.0(9)	−157.9(11)	175.8(4)
C(123)–S(13)–C(131)–C(132)	169.9(7)	164.1(10)	128.0(11)	−179.2(4)
S(13)–C(131)–C(132)–C(133)	62.3(10)	60.7(12)	71.3(13)	76.7(5)
C(131)–C(132)–C(133)–S(14)	−63.4(10)	−61.0(12)	−65.7(13)	−76.8(5)
C(132)–C(133)–S(14)–C(141)	−163.5(8)	−168.9(9)	169.1(10)	179.1(4)
C(133)–S(14)–C(141)–C(142)	168.8(8)	172.8(10)	−167.6(10)	−175.6(4)
S(14)–C(141)–C(142)–C(143)	62.9(11)	60.5(14)	66.9(14)	77.0(5)
C(141)–C(142)–C(143)–S(11)	−66.6(10)	−63.7(13)	−72.1(14)	−78.6(5)
C(142)–C(143)–S(11)–C(111)	−162.8(7)	−158.6(10)	−130.2(10)	179.7(4)
C(143)–S(11)–C(111)–C(112)	173.6(7)	167.0(9)	152.9(10)	−176.4(4)

[a] e.s.d. less than 0.05. [b] Corresponding values for *trans*-[$MoBr_2(Me_8[16]aneS_4)$].[2]

Table 5 Comparison of the co-ordination patterns of the Mo and W atoms in complexes **1**, **3** and **4**

	Capped octahedral		Capped trigonal prismatic		
Complex	Capping ligand	r.m.s. angular deviation*	Capping ligand	r.m.s. angular deviation*	Ref.
1, cation	S(14)	7.3	Br(15)	4.1	This work
anion	C(27)	1.4	Br(23)	7.2	
3, cation	S(13)	9.4	I(15)	3.5	This work
anion	C(27)	1.0	I(22)	7.4	
4, cation	C(17)	5.3	I(15)	5.9	This work
anion	C(27)	2.1	I(23)	6.8	
$[WBr_3(CO)_4]^-$	C(2)	0.7	Br(2)	7.0	19
$[Mo(CNBu)_7]^{2+}$	C(41)	7.6	C(11)	0.7	20

* From the 'ideal' values for the capped-octahedral and capped-trigonal-prismatic geometries, *i.e.* those with 3*m* and *mm*2 symmetries respectively.[24] The last two complexes are included as examples having well defined geometries.

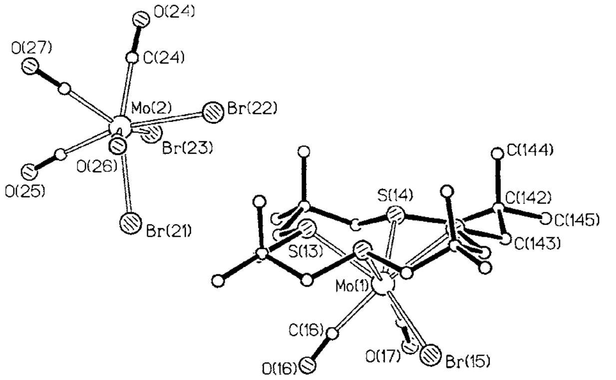


Fig. 1 Structure of $[MoBr(CO)_2(Me_8[16]aneS_4)][MoBr_3(CO)_4]$ **1**. The minor component of the bromide ligand and the atoms of the unresolved solvent molecules(s) are not shown

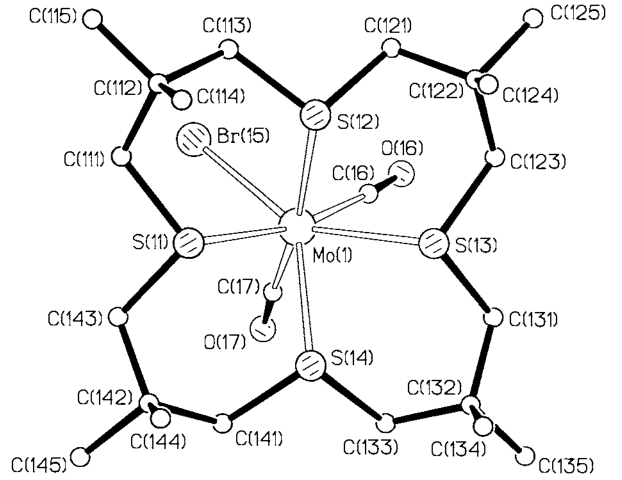


Fig. 2 The cation of complex **1**, showing the atom numbering scheme of the macrocyclic ligand, common also to that in **3** and **4**

(each value is the mean of the eight related by the pseudo-4*mm* symmetry); in *trans*-$[MoBr_2(Me_8[16]aneS_4)]$ the corresponding values of g and t are 77.6(4) and −177.9(6) [*i.e.* +182.1(6)°], *i.e.* there is a difference of *ca.* 14° in the twist about each bond, allowing the S-atoms to bond the Mo in the S_4 plane rather than *ca.* 1.5 Å out of that plane.

The seven-co-ordinate anion $[MoBr_3(CO)_4]^-$, which as far as we are aware has not been previously structurally characterised, has a capped-octrahedral structure (Table 5) and is isostructural with the tungsten analogues, $[WX_3(CO)_4]^-$ (X = Br or I).[19,21] The anion has a carbonyl ligand, C(27), capping a trigonal face of carbonyl ligands, and the three bromide ligands form the opposite face.

The ^1H NMR spectrum of complex **1** in CD_2Cl_2 solution shows five overlapping singlets in the methyl region, suggesting that the cation's approximate C_s symmetry is retained in solution; in this case the eight methyl groups of $Me_8[16]aneS_4$ should give a total of six signals (the sixth is probably overlapped by the hexane resonance at δ 1.23). This contrasts with complexes such as *trans*-$[Mo(CO)_2(Me_8[16]aneS_4)]$[9] where the equatorial co-ordination geometry of the macrocycle means that the methyl groups are distinguished as two sets of four, giving two singlets in the ^1H NMR spectrum. The CH_2 groups in **1** give rise to a very broad set of resonances at δ 3.2–2.4.

Heating a suspension of complex **1** in toluene under reflux for 3 h gave *trans*-$[MoBr_2(Me_8[16]aneS_4)]^2$ in 31% yield, suggesting that **1** may be an intermediate in the direct preparation of the latter from $[\{Mo(\mu\text{-}Br)Br(CO)_4\}_2]$.[9] The non-methylated analogue of **1**, $[MoBr(CO)_2([16]aneS_4)][MoBr_3(CO)_4]$, can be prepared from $[16]aneS_4$ and $[\{Mo(\mu\text{-}Br)Br(CO)_4\}_2]$ by an analogous procedure,[22] but appears to be prone to rapid decomposition in solution.

Reaction of equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and $Me_8[16]aneS_4$ in CH_2Cl_2 at 20 °C gave a mixture of products plus starting material. However, the reaction of 2 equivalents of $[MoI_2(CO)_3(NCMe)_2]$ with 1 of $Me_8[16]aneS_4$ under the same conditions gave the complex $[MoI(CO)_2(Me_8[16]aneS_4)][MoI_3(CO)_4]$ **2**, whilst the analogous reaction with $[WI_2(CO)_3(NCMe)_2]$ afforded two complexes $[WI(CO)_2(Me_8[16]aneS_4)][WI_3(CO)_4]$ **3** and $[WI(CO)_3(Me_8[16]aneS_4)][WI_3(CO)_4]$ **4**, which were separated by fractional crystallisation. Complexes **1**–**4** are soluble in chlorinated solvents, acetone, acetonitrile and related solvents, but insoluble in diethyl ether and hexane. As with all the complexes described in this work, they are air-sensitive both in the solid state and in solution, but can be stored under dinitrogen in the dark for several days without appreciable decomposition. The molar conductivities of complexes **2** and **3** (70 and 75 Ω^{-1} cm^2 mol^{-1} respectively) show them to be 1 : 1 electrolytes in nitromethane.

The IR spectra of complexes **1**–**4** in the carbonyl region may be compared to those of $[NEt_4][WBr_3(CO)_4]$,[18] the *N*-methylpyridinium salts $[C_5H_5NMe][MI_3(CO)_4]$ (M = Mo or W)[23] and the cationic tricarbonyl complexes $[MI(CO)_3([9]aneS_3)]I$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane, M = Mo or W)[24] (see Fig. 3). The $[MX_3(CO)_4]^-$ anion, ideal symmetry C_{3v}, gives three carbonyl IR bands in solution,[18] split into five in the solid state.[23] The highest frequency of these can be distinguished in the spectra of all the complexes containing an $[MX_3(CO)_4]^-$

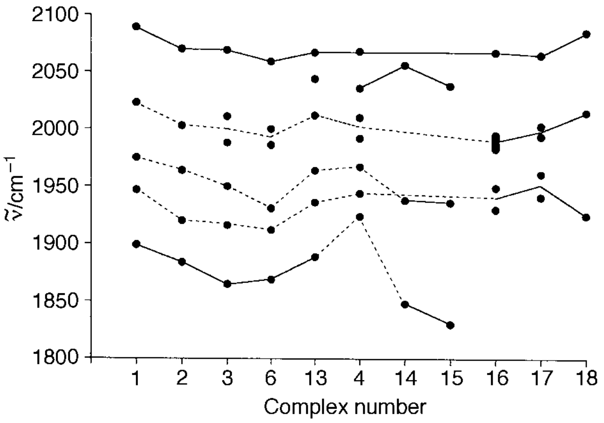


Fig. 3 Infrared data for the ionic complexes in the carbonyl region. Complex numbers are as in Table 1; additional data for $[MI(CO)_3([9]aneS_3)]^+$ (M = Mo **14** or W **15**),[24] $[MI_3(CO)_4]^-$ (M = W **16** or Mo **17**)[23] and $[WBr_3(CO)_4]^-$ **18**[18] were taken from the literature. Solid and broken lines indicate probable and possible correlations respectively

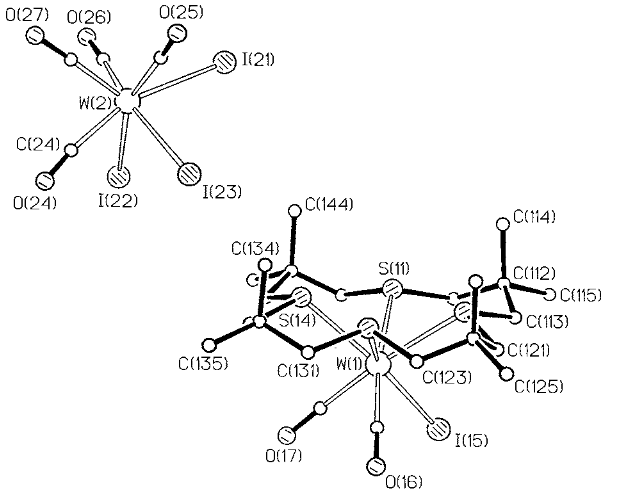


Fig. 4 Structure of $[WI(CO)_2(Me_8[16]aneS_4)][WI_3(CO)_4]$ **3**

anion in the present study, whilst the lowest-frequency carbonyl band in their spectra can be assigned to the corresponding cation. Assignments of the intermediate-frequency bands to the cation or anion are more tentative, though comparison of the spectrum of **4** with that of $[MI(CO)_3([9]aneS_3)]^+$ (M = Mo or W) suggests that the band at 2036 cm^{-1} in the spectrum of **4** arises from the extra carbonyl ligand of its cation compared to the cations of **1**–**3**.

The room-temperature ^1H NMR spectra of complexes **2** and **3** in $CDCl_3$ both show multiplets between δ 1.7 and 1.5, indicating that, as for **1**, the C_s symmetry of the cation in the crystal structure is preserved in solution. The room-temperature ^{13}C NMR spectrum of **3** in CD_2Cl_2 showed two carbonyl resonances at δ 233 and 201; the two carbonyls of the cation are expected to be equivalent, whilst the anion is likely to be fluxional in solution. The UV–VIS spectrum of **3** in CH_2Cl_2 showed bands at 630, 410 and 323 nm, which are probably d–d transitions, and a band at 230 nm which may be due to ligand-to-metal charge transfer.

The molecular structures of complexes **3** and **4** have been determined by X-ray analysis. Single crystals of both were grown by fractional crystallisation of a cooled solution (−17 °C) in CH_2Cl_2. The structure of **3** is shown in Fig. 4 and that of **4** in Fig. 5; selected bond lengths and angles for both are in Table 4. As in complex **1** the metal atoms in both the cation and anion of each complex are seven-co-ordinate.

The cation of complex **3** is another example of 'piano-stool' co-ordination of $Me_8[16]aneS_4$ and is very similar to that of **1**. The cation is best described as having distorted capped-trigonal-prismatic co-ordination, with I(15) as the capping ligand on the rectangular face of S(11), S(12), C(16) and C(17); the opposite edge of the prism is S(13)–S(14) (see later and Table 5). As in complex **1** the cation is disordered; the W–I bond in the major component [I(15) has an occupancy of *ca.* 85%] lies above the S(11)···S(12) midpoint (projecting the cation on to the S_4 plane); in the minor component, the W(1)–I(15′) bond lies over the midpoint of S(12)···S(13), and I(15′) is the capping ligand in a similarly distorted capped-trigonal-prismatic co-ordination pattern. In both major and minor conformations the cation has a pseudo-mirror plane of symmetry which passes through the W and I atoms; the pairs of carbonyl groups and the macrocyclic ligand conform closely to this symmetry in each component.

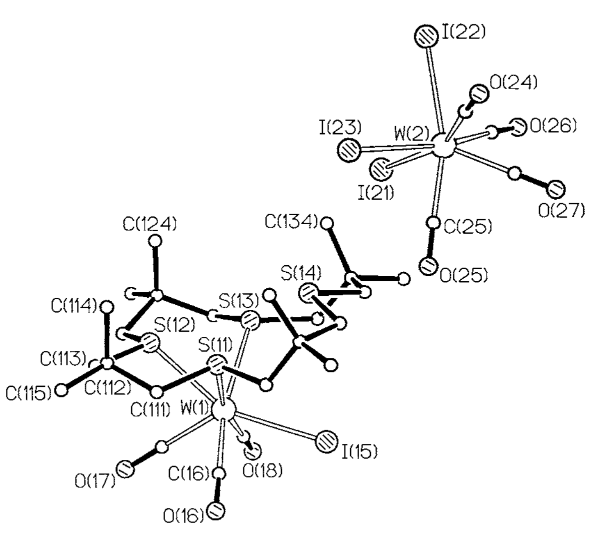


Fig. 5 Structure of $[WI(CO)_3(Me_8[16]aneS_4)][WI_3(CO)_4]$ **4**

In comparison with complex **1**, the W atom of the cation of **3** lies 1.506(2) Å from the good mean plane of the four S atoms [each S atom < 0.061(4) Å from the mean plane], the pseudo-four-fold symmetry of the macrocycle is maintained with the corresponding mean torsion angles, g and t, of 63.8(12) and 166.4(17), and the mean adjacent S···S distance is 2.97(2) Å.

The cation of complex **4** exhibits *S,S′,S″*-$Me_8[16]aneS_4$ ligation and, to our knowledge, is the first example of this binding mode structurally established in a mononuclear complex.[17] One example of such ligation has been found for the related macrocycle $[14]aneS_4$ in the polymeric compound $[\{Cu(\mu\text{-}[14]aneS_4)\}_n]$, which has the fourth sulfur bound to a second metal.[25] In **4** the fourth sulfur atom of the ring is turned away from the metal atom, giving a W(1)···S(14) distance of 4.047(4) Å. A co-ordination number of seven is retained in the cation of **4** by retention of an extra carbonyl ligand compared to **1** and **3**. It should be noted that **4** contains more carbonyl ligands per W atom than does the starting complex, and must therefore be produced using CO released *via* the generation of other products.

In the cation of complex **4** the geometry about the W atom is intermediate between capped octahedral and capped trigonal prismatic. There is approximate mirror symmetry in the ion, with the mirror plane passing through I(15), S(12) and S(14). Considering the pattern as distorted capped octahedral, the carbonyl group of C(17) caps a plane of S(12), C(16) and C(18); the iodide and remaining S atoms are in the opposite plane. In the distorted capped-trigonal-prismatic description I(15) is the capping ligand, but the W–I bond is displaced considerably from the normal to the mean plane of S(11), S(13), C(16) and C(18). We have calculated the root-mean-square (r.m.s.) deviations of these distorted geometries from the idealised patterns and our results for this and related complexes[19,20] are listed in Table 5; they confirm our description for **4**. Also, the '4:3 piano-stool' arrangements for the cations of complexes **1** and **3** are, from these calculations, shown in the more standard descriptions to be closer to the capped-trigonal-prismatic pattern. The anions of **1**, **3** and **4** are closely isostructural, with well defined capped-octahedral geometries; the ligand of C(27) in each anion caps the face of the other three carbonyl groups, and is opposite the face of the three halides. In complex **4** the mean value of the W–S bond length to the co-ordinated sulfur atoms is 2.586(20) Å, which is comparable to the mean Mo–S length of 2.586(16) Å in **1** and to the mean W–S length of 2.585(15) Å in **3**; there is a range of *ca.* 0.07 Å in the values for each complex. The observation that the macrocycle is able to deform itself to achieve essentially identical M–S bond lengths in the S_3- and S_4-facial co-ordination modes, allowing for the additional steric constraint of accommodating the extra carbonyl ligand in **4**, provides another example of the great co-ordination flexibility of sulfur macrocycles.[8,16] The macrocycle in complex **4** has torsion angles in the co-ordinated section of the ring of similar values to those in **1** and **3**, but there is a pair of values, on opposite sides of the mirror plane, of ± *ca.* 130° which takes S(14) out of range of a W–S bonding contact. The S · · · S distances fall into two groups; the pair about S(12), with a mean value of 2.874(14) Å, and the pair about S(14), mean 3.107(4) Å.

The W–I bond length of 2.806(1) Å in the cation of **4** is within the range we have found in the cations of other seven-co-ordinate complexes of tungsten(II) {*e.g.* 2.755(1) Å in **3** and 2.818(1) Å in $[WI(CO)_3([9]aneS_3)][BPh_4]$[24]}, and a little shorter than those observed in corresponding neutral complexes {*e.g.* a mean value of 2.855(3) Å in $[WI_2(CO)_3(NCMe)(PPh_3)]$[24]} and in anionic complexes [*e.g.* mean values of 2.855(2) and 2.855(9) Å in **3** and **4**].

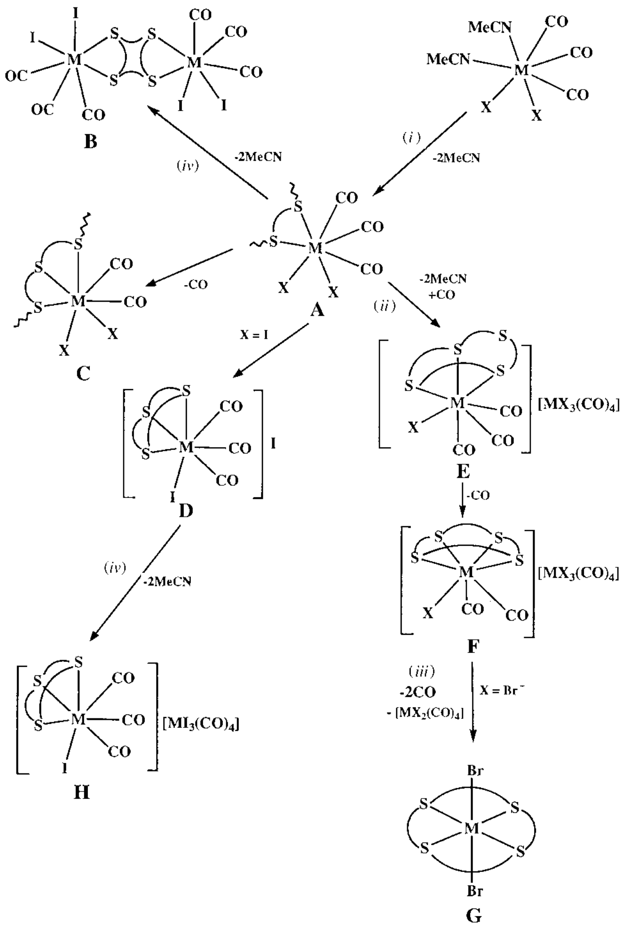
The reactivities of complexes **1** and **3** with a number of reagents such as zinc, butyllithium, dibromine and tetraethylammonium bromide were investigated, but no characterisable products incorporating $Me_8[16]aneS_4$ were obtained. It appears that the macrocycle is much more labile when co-ordinated in the facial geometry compared to the equatorial geometry; this is borne out by the reaction of **1** with donor solvents such as acetonitrile at room temperature to give free $Me_8[16]aneS_4$.

The reaction of $[MoI_2(CO)_3(NCMe)_2]$ with 1 equivalent of $[16]aneS_4$ in CH_2Cl_2 at 20 °C gave the dinuclear product $[Mo_2I_4(CO)_6(\mu\text{-}[16]aneS_4\text{-}S,S',S'',S''')]$ **5**, whilst reaction of 2 equivalents of $[WI_2(CO)_3(NCMe)_2]$ with 1 equivalent of $[16]aneS_4$ under the same conditions gave $[WI(CO)_2([16]aneS_4)][WI_3(CO)_4]$ **6**. Complex **5** was found to be non-conducting in dimethylformamide (dmf), whereas **6** is a 1 : 1 electrolyte in nitromethane with a conductance value of 77 Ω^{-1} cm^2 mol^{-1}.

As indicated above, the macrocycle in complex **5** probably acts as a doubly bridging ligand between the two molybdenum centres (see Scheme 1, structure **B**). Examples of similar complexes include $[Mo_2(CO)_6(\mu\text{-}[18]aneS_6)]$ ($[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane),[15,26] where the macrocycle co-ordinates in a doubly tridentate bridging manner between the two $Mo(CO)_3$ units, and the seven co-ordinate complex $[Mo_2I_4(CO)_6(\mu\text{-}[18]aneS_6)]$.[15]

The IR spectrum of complex **5** showed three carbonyl stretching bands at 2069, 1994 and 1910 cm^{-1}, similar to those of $[Mo_2(CO)_6(\mu\text{-}[18]aneS_6)]$[15] at 1920, 1820 and 1790 cm^{-1}. The room-temperature ^{13}C NMR spectrum in $[^2H_7]dmf$ showed one carbonyl resonance at δ 235.9, suggesting that it is fluxional; at 223 K three resonances were observed, at δ 236.4, 214.7 and 205.1, suggesting that the two molybdenum centres are identical. These data are very similar to those obtained for the crystallographically characterised, capped-octahedral complex $[WI_2(CO)_3\{(4\text{-}MeC_6H_4SCH_2)_2\}]$,[27] which gave a single resonance at δ 218.6 at room temperature and three, δ 235.2, 210.8 and 208.9, at 208 K.

The spectroscopic properties of complex **6** are very similar to those of the $Me_8[16]aneS_4$ analogue **3** (see Fig. 3), hence it probably has an analogous structure. An attempt to improve its yield by the reaction of $[\{W(\mu\text{-}I)I(CO)_4\}_2]$ with $[16]aneS_4$ was unsuccessful, perhaps due to the instability of $[\{W(\mu\text{-}I)I(CO)_4\}_2]$.[28]



Scheme 1 M = Mo or W, X = Br or I. (*i*) S_n ligand (*n* = 2–4); (*ii*) $[MX_2(CO)_3(NCMe)_2]$; (*iii*) heat; (*iv*) $[MI_2(CO)_3(NCMe)_2]$

In a search for alternative routes to the chemistry of molybdenum complexes of $[16]aneS_4$ we investigated the reaction of this macrocycle with the six-co-ordinate starting material $[MoCl_3(thf)_3]$. Reaction of $[16]aneS_4$ with an equimolar quantity of $[MoCl_3(thf)_3]$ in CH_2Cl_2 at 20 °C gave a purple solution, from which a purple solid (complex **7**) precipitated over the course of several days. After an extended reaction time (1 month) a second product (**8**) was precipitated by addition of hexane. The microanalytical data for **7** and **8** are consistent with their formulation as $[Mo_3Cl_9([16]aneS_4)_2]\cdot0.5CH_2Cl_2$ and $[Mo_2Cl_5([16]aneS_4)_2]Cl\cdot0.33C_6H_{14}$ respectively. Although both complexes are paramagnetic, the presence of solvent of crystallisation was confirmed by NMR spectroscopy after decomposition with $(CD_3)_2SO$. The structural formulae of **7** and **8** can be deduced by consideration of the reactions undergone by $[MoCl_3(thf)_3]$ in CH_2Cl_2, which have been described by Poli and Mui.[29] These authors showed by NMR spectroscopy that *mer*-$[MoCl_3(thf)_3]$, initially present in solution, eliminates thf to give at first the chloride-bridged dimer $[\{Mo(\mu\text{-}Cl)Cl_2(thf)_2\}_2]$, followed by the asymmetric, confacial bioctahedral complex $[\{MoCl_2(thf)\}(\mu\text{-}Cl)_3\{MoCl(thf)_2\}]$. Substitution of thf by $[16]aneS_4$ in *mer*-$[MoCl_3(thf)_3]$ and $[\{Mo(\mu\text{-}Cl)Cl_2(thf)_2\}_2]$ would give the polymeric structure for **7** shown in Fig. 6(*a*), whilst $[\{MoCl_2(thf)\}(\mu\text{-}Cl)_3\{MoCl(thf)_2\}]$ could react with $[16]aneS_4$ to give **8**, with the dinuclear structure shown in Fig. 6(*b*), *via* substitution of thf and ionisation of one chloride ligand. Further evidence for the proposed formulation for **8** is provided by its reaction with $Na[BPh_4]$ to give $[Mo_2Cl_5([16]aneS_4)_2][BPh_4]$ **9** (Table 1).

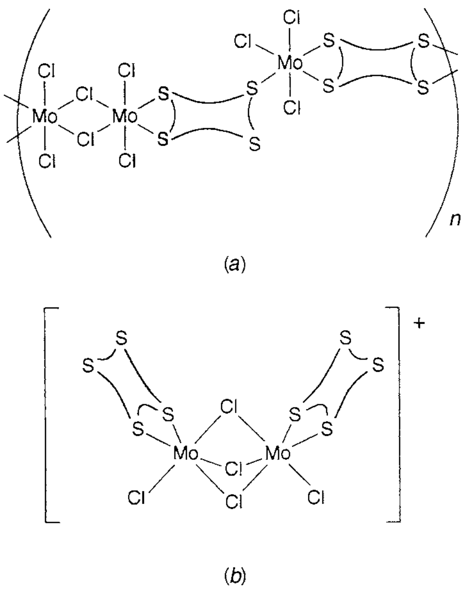


Fig. 6 Proposed structures of [{Mo_3Cl_9([16]aneS_4)$_2$}$_n$] **7** (*a*) and [Mo_2Cl_5([16]aneS_4)$_2$]$^+$ **8** (*b*)

Complex **7** is insoluble in all but strongly co-ordinating solvents such as Me_2SO, consistent with its polymeric structure. It is related to the polymeric compounds [{$MoCl_3$(thf)([14]aneS_4)}$_n$] and [{Mo_2Cl_6([14]aneS_4)$_2$}$_n$] described by Sevdić and Fekete.[3] Formation of such polymeric species, which are readily precipitated, is doubtless facilitated by the preference of free [16]aneS_4 and [14]aneS_4 for endodentate conformations,[8,30] well suited to bridging co-ordination modes. The reaction of [$MoCl_3$(thf)$_3$] with Me_8[16]aneS_4 was also investigated, but no identifiable product could be isolated.

[14]aneS_4 complexes

Reaction of 1 or 2 equivalents of [$MI_2(CO)_3(NCMe)_2$] (M = Mo or W) with 1 equivalent of [14]aneS_4 in CH_2Cl_2 at 20 °C gave the complexes [$M_2I_4(CO)_6$(μ-[14]aneS_4-*S*,*S*′,*S*″,*S*‴)] **10** and **11** respectively. Their molar conductivities in dmf (15 and 8 Ω^{-1} cm^2 mol^{-1} respectively) showed them to be non-conducting. On the basis of their physicochemical and spectroscopic properties they may be formulated as dimers, analogous to complex **5** described above. Related dimeric, five-co-ordinate, zerovalent complexes [$M_2(CO)_6$([14]aneS_4)] (M = Mo[15] or W[31]) have been reported.

[12]aneS_4 complexes

The reaction of [$MoI_2(CO)_3(NCMe)_2$] with 1 equivalent of [12]aneS_4 in CH_2Cl_2 at 20 °C gave the macrocycle-bridged dimer [$Mo_2I_4(CO)_6$(μ-[12]aneS_4-*S*,*S*′,*S*″,*S*‴)] **12**, whereas reaction of 2 equivalents of [$WI_2(CO)_3(NCMe)_2$] with one of [12]aneS_4 under the same conditions afforded the ionic complex [$WI(CO)_2$([12]aneS_4)][$WI_3(CO)_4$] **13**. As expected, complex **12** was found to be non-conducting in dmf, whereas **13** gave a conductivity of 80 Ω^{-1} cm^2 mol^{-1} in nitromethane, consistent with a 1 : 1 electrolyte. It is interesting that in contrast to [14]aneS_4 the products of the reactions of [12]aneS_4 with [$MI_2(CO)_3(NCMe)_2$] are exactly analogous to those obtained from the latter with [16]aneS_4. Since the spectroscopic properties of **12** and **13** are very similar to those of **5** and **6** respectively it is likely that they will have closely related structures. It may be noted from Fig. 3, however, that the carbonyl band at 2044 cm^{-1} in the IR spectrum of **13** could be due to the presence of an extra carbonyl ligand in the cation in a structure analogous to that of **4**, *i.e.* [$WI(CO)_3$([12]aneS_4)][$WI_3(CO)_4$]; this possibility would give an equally good fit to the microanalytical data.

Conclusion

The results of the present study, along with those of our earlier reports on di- and tri-thioether complexes,[24,27,32] are summarised in Scheme 1. For all the polythioethers studied the first step in their reaction with [$MI_2(CO)_3(NCMe)_2$] (M = Mo or W) is probably displacement of the two substitution labile acetonitrile ligands to give a bidentate-*S*,*S*′ complex **A**. A crystallographically characterised example of such a complex of an acyclic dithioether is [$WI_2(CO)_3${(4-$MeC_6H_4SCH_2$)$_2$}];[27] in addition, Blake *et al.*[33] have recently reported the crystal structures of [$PdCl_2$([18]aneS_2O_4)], [Pd([18]aneS_2O_4)$_2$]$^{2+}$ and [Pd([18]aneS_3O_3)$_2$]$^{2+}$ ([18]aneS_2O_4 = 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane, [18]aneS_3O_3 = 1,4,7-trioxa-10,13,16-trithiacyclooctadecane) in which the mixed S/O macrocycles act as bidentate ligands through two neighbouring sulfur atoms. It may be noted that where [{Mo(μ-Br)Br$(CO)_4$}$_2$] is the precursor complex its homolytic cleavage accompanied by reaction with the macrocycle and loss of CO would give **A** (M = Mo, X = Br), whereas heterolytic cleavage and loss of CO would lead directly to **E** (M = Mo, X = Br). Whilst either alternative seems possible for the formation of complex **1**, the first route would better explain the preparation of [$MoBr_2(CO)_2$(ttob)] (ttob = 2,5,8-trithia-[9]-*o*-benzenophane) from [{Mo(μ-Br)Br$(CO)_4$}$_2$] and ttob.[32]

If the thioether ligand in complex **A** contains more than two sulfur atoms it is able to undergo further reaction in a variety of ways. Reaction with a second molecule of [$MI_2(CO)_3(NCMe)_2$] generates the dinuclear species **B**; it seems unlikely, however, that Me_8[16]aneS_4 could achieve this co-ordination mode, due to the extra steric constraints of its methyl substituents. Complex **A** can also react further, either by loss of CO or by ionisation of X^-, allowing the polythioether ligand to become tridentate (structures **C**–**E**). A crystallographically characterised example of structure **C** is furnished by [$WI_2(CO)_2${S(CH_2CH_2SMe)$_2$}].[27] Whilst loss of halide from **A** to give complex **D** is apparently spontaneous for complexes such as [$WI(CO)_3$([9]aneS_3)]I,[24] in other cases it may be assisted by formation of the [$MX_3(CO)_4$]$^-$ anion to give **E** (as in complex **4**) and **H** {exemplified by [$WI(CO)_3$(ttob)][$WI_3(CO)_4$]}.[24] Apart from the steric factors noted above, there seems to be no obvious relationship between the nature of **A**, in terms of metal, halide and macrocycle, and the preferred reaction pathway.

For tetrathioether ligands, complex **E** can eliminate CO to allow co-ordination of the final sulfur, giving **F**. Finally, the observation that **G** can be prepared from **F** suggests that halide may approach the metal atom through the central cavity of the macrocyclic ligand, which simultaneously takes up an equatorial co-ordination mode. Until that point the macrocycle is relatively weakly bound; once it is girdling the metal, as in complex **G**, it is likely to be much harder to displace.

Experimental

All the reactions described were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. The starting materials [{Mo(μ-Br)Br$(CO)_4$}$_2$],[34] [$MI_2(CO)_3(NCMe)_2$] (M = Mo or W)[35] and Me_8[16]aneS_4[30] were prepared according to the literature procedures. All other chemicals were obtained from commercial sources and used without further purification.

Proton NMR spectra were recorded on Bruker AC/250 or JEOL GSX 270 spectrometers, ^{13}C NMR spectra on Bruker WH 400 MHz or JEOL GSX 270 spectrometers, referenced to tetramethylsilane. Infrared spectra were recorded on Perkin-Elmer 1600 series FTIR and 883 series grating spectrophotometers. Elemental analyses were determined using a Carlo-Erba MOD 1106 instrument (He as carrier gas) for C, H, N, at Bangor and for S at Norwich. Conductivities were measured using a Portland Electronics conductivity bridge.

Preparations

[MoBr(CO)$_2$(Me$_8$[16]aneS$_4$)][MoBr$_3$(CO)$_4$] 1. Dichloromethane (20 cm^3) was added to a solid mixture of freshly prepared [{Mo(μ-Br)Br(CO)$_4$}$_2$] (0.34 g, 0.46 mmol) and Me$_8$[16]aneS$_4$ (0.39 g, 0.95 mmol). The mixture was stirred for 18 h, giving an emerald-green solution. This was concentrated *in vacuo* to *ca*. 10 cm^3; addition of hexane (25 cm^3) gave a precipitate, which was filtered off, washed with hexane and dried *in vacuo* (yield: 0.37 g, 74% based on [{Mo(μ-Br)Br(CO)$_4$}$_2$]).

[MI(CO)$_2$(Me$_8$[16]aneS$_4$)][MI$_3$(CO)$_4$] (M = Mo 2 or W 3) and [WI(CO)$_3$(Me$_8$[16]aneS$_4$)][WI$_3$(CO)$_4$] 4. To a solution of [WI$_2$(CO)$_3$(NCMe)$_2$] (0.30 g, 0.497 mmol) in CH$_2$Cl$_2$ (25 cm^3) was added Me$_8$[16]aneS$_4$ (0.11 g, 0.269 mmol). The mixture was stirred for 18 h and the solvent removed *in vacuo* to produce a green powder, which was redissolved in CH$_2$Cl$_2$. The solution was filtered, reduced to a minimum volume and cooled to −17 °C for 24 h to give crystals of a mixture of products. These were separated by fractional crystallisation at −17 °C to give crystals suitable for X-ray crystallography. These were the green complex [WI(CO)$_2$(Me$_8$[16]aneS$_4$)][WI$_3$(CO)$_4$] **3** (yield: 0.5 g, 35%) and the orange complex [WI(CO)$_3$(Me$_8$[16]aneS$_4$)]-[WI$_3$(CO)$_4$] **4** (yield: 0.26 g, 18%).

A similar reaction of 2 equivalents of [MoI$_2$(CO)$_3$(NCMe)$_2$] with 1 of Me$_8$[16]aneS$_4$ followed by recrystallisation from CH$_2$Cl$_2$ at −17 °C gave [MoI(CO)$_2$(Me$_8$[16]aneS$_4$)][MoI$_3$(CO)$_4$] **2** (yield: 0.48 g, 32%).

[M$_2$I$_4$(CO)$_6$(μ-[*n*]aneS$_4$-*S,S′,S″,S‴*)] (M = Mo, *n* = 16, 5; *n* = 14, 10; *n* = 12, 12; M = W, *n* = 14, 11). To a solution of [MoI$_2$(CO)$_3$(NCMe)$_2$] (0.30 g, 0.582 mmol) in CH$_2$Cl$_2$ (25 cm^3) was added [16]aneS$_4$ (0.18 g, 0.607 mmol). The mixture was stirred for 18 h, giving a brown precipitate. This was filtered off, washed with Et$_2$O and dried *in vacuo* to produce [Mo$_2$I$_4$(CO)$_6$(μ-[16]aneS$_4$-*S,S′,S″,S‴*)] **5** in analytically pure form (yield; 0.43 g, 32%).

Using the same procedure and molar quantities but [14]aneS$_4$ or [12]aneS$_4$ in place of [16]aneS$_4$ gave [Mo$_2$I$_4$(CO)$_6$(μ-[14]aneS$_4$-*S,S′,S″,S‴*)] **10** (yield: 0.40 g, 30%) and [Mo$_2$I$_4$(CO)$_6$(μ-[12]aneS$_4$-*S,S′,S″,S‴*)] **12** (yield: 0.43 g, 32%) respectively. The analogous procedure using [WI$_2$(CO)$_3$(NCMe)$_2$] and [14]aneS$_4$ gave [W$_2$I$_4$(CO)$_6$(μ-[14]aneS$_4$-*S,S′,S″,S‴*)] **11** (yield: 0.45 g, 35%). Reaction of [MoI$_2$(CO)$_3$(NCMe)$_2$] (0.60 g, 1.163 mmol) with [14]aneS$_4$ (0.16 g, 0.582 mmol) in CH$_2$Cl$_2$ (30 cm^3) at 20 °C also gave complex **10** (yield: 1.0 g, 38%); using the same procedure and molar quantities but [WI$_2$(CO)$_3$(NCMe)$_2$] in place of [MoI$_2$(CO)$_3$(NCMe)$_2$] gave **11** (yield: 1.07 g, 41%).

[WI(CO)$_2$([16]aneS$_4$)][WI$_3$(CO)$_4$] 6. Solid [16]aneS$_4$ (0.08 g, 0.270 mmol) was added to a stirred solution of [WI$_2$(CO)$_3$(NCMe)$_2$] (0.30 g, 0.497 mmol) in CH$_2$Cl$_2$ (25 cm^3), and the resulting green solution was stirred at 20 °C for 18 h. The solvent was removed *in vacuo* to give a powder, which was recrystallised from CH$_2$Cl$_2$ as the analytically pure complex [WI(CO)$_2$-([16]aneS$_4$)][WI$_3$(CO)$_4$] **6** (yield: 0.40 g, 30%).

[Mo$_3$Cl$_9$([16]aneS$_4$)$_2$]·0.5CH$_2$Cl$_2$ 7 and [Mo$_2$Cl$_5$([16]aneS$_4$)$_2$]-Cl·0.33C$_6$H$_{14}$ 8. Dichloromethane (30 cm^3) was added to a solid mixture of freshly prepared [MoCl$_3$(thf)$_3$] (2.8 g, 6.7 mmol) and [16]aneS$_4$ (2.0 g, 6.7 mmol), giving a dark brown solution. This was stirred at 20 °C for 72 h, then filtered; the purple solid was washed with CH$_2$Cl$_2$ and dried *in vacuo*, giving [Mo$_3$Cl$_9$([16]aneS$_4$)$_2$]·0.5CH$_2$Cl$_2$ **7** (yield: 1.49 g, 54% based on Mo). Infrared spectrum (CsI disc): 2930w, 1435m, 1360m, 1266m, 1015w, 853w, 734m, 695w and 330s cm^{-1}. The filtrate was left to stand for 1 month, then filtered again and diluted with an equal volume of hexane. The resulting solid was filtered off, washed with hexane and dried *in vacuo* to give [Mo$_2$Cl$_5$([16]aneS$_4$)$_2$]Cl·0.33C$_6$H$_{14}$ **8** (yield: 1.37 g, 40% based on Mo). Infrared spectrum (CsI disc): 2925m, 1442m, 1416m, 1254m, 855w, 760w and 325s cm^{-1}.

[Mo$_2$Cl$_5$([16]aneS$_4$)$_2$][BPh$_4$]·Et$_2$O 9. A solution of Na[BPh$_4$] (0.16 g, 0.46 mmol) in thf (30 cm^3) was added to solid [Mo$_2$Cl$_5$([16]aneS$_4$)$_2$]Cl (0.22 g, 0.22 mmol) and the resulting mixture was stirred at 20 °C for 2 h, then filtered. The filtrate was concentrated *in vacuo* to *ca*. 5 cm^3 and Et$_2$O (10 cm^3) was added, giving a purple oil. The supernatant was decanted off and the residue dried *in vacuo*, giving [Mo$_2$Cl$_5$([16]aneS$_4$)$_2$]-[BPh$_4$]·Et$_2$O **9** (yield: 0.12 g, 42%). Infrared spectrum (CsI disc): 2990w, 1482w, 1430w, 1361w, 1243w, 1050m, 853m, 747s, 713s, 615m, 607m, 348s and 316s cm^{-1}.

[WI(CO)$_2$([12]aneS$_4$)][WI$_3$(CO)$_4$] 13. A solution of [12]aneS$_4$ (0.07 g, 0.291 mmol) and [WI$_2$(CO)$_3$(NCMe)$_2$] (0.32 g, 0.530 mmol) in CH$_2$Cl$_2$ (25 cm^3) was stirred at 20 °C for 16 h. The solvent was removed *in vacuo* to give a powder, which was recrystallised from CH$_2$Cl$_2$–Et$_2$O as the analytically pure complex [WI(CO)$_2$([12]aneS$_4$)][WI$_3$(CO)$_4$] **13** (yield: 0.52 g, 38%).

Crystallography

Complexes **1**, **3** and **4** were analysed by X-ray diffraction methods following very similar procedures. Crystal data for the three samples and details of the experimental results are shown in Table 6.

For each sample, crystals were mounted, in air, on glass fibres and examined photographically before transfer to an Enraf-Nonius CAD4 diffractometer (equipped with monochromated Mo-Kα radiation, λ 0.710 69 Å). Accurate cell parameters were determined by refinement from the settings of 25 reflections (θ 10–11°), each reflection being centred in four orientations. Diffraction intensities were measured at 20 °C using an ω–θ scan method.

During processing corrections were applied for Lorentz-polarisation effects, crystal deterioration (for complexes **1** and **3**), absorption (by semi-empirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods). The structure of each compound was determined by the automated Patterson routines in the SHELXS program[37] and refined (on *F*) by large-block-matrix least-squares methods in the program SHELX 76.[36] Hydrogen atoms were included in idealised positions; the methyl group atoms in **3** and **4** were refined with geometrical constraints. The non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen U_{iso} values in **3** and **4** were allowed to refine freely, but those in **1** were set to ride on those of the parent C atoms. In the cations of **1** and **3** there is site disorder of the halide and the two carbonyl ligands; in each case there is one principal site (*ca*. 95% in **1**, 85% in **3**) and one minor site, but the carbonyl atoms in the minor sites in **1** were not located. The atoms of the minor bromide ligand in **1** and the minor carbonyl groups in **3** were refined isotropically. In **1** there is also a molecule of solvent, hexane, which is not fully resolved; carbon atoms in partially occupied sites were refined isotropically.

Scattering factors for neutral atoms in each analysis were taken from ref. 38. Computer programs used in this analysis have been noted above or in Table 4 of ref. 39, and were run on a DEC MicroVAX 3600 computer in the Nitrogen Fixation Laboratory, University of Sussex.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/335.

Table 6 Crystal data and experimental crystallographic details for complexes **1**, **3** and **4**

	1	**3**	**4**
Elemental formula	$C_{22}H_{40}BrMoO_2S_4$, $C_4Br_3MoO_4{\cdot}C_6H_{14}$	$C_{22}H_{40}IO_2S_4W$, $C_4I_3O_4W$	$C_{23}H_{40}IO_3S_4W$, $C_4I_3O_4W$
M	1174.5	1452.2	1480.2
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$F2/d$ (equivalent to no. 15)	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)
a/Å	24.279(2)	11.646(1)	12.449(2)
b/Å	19.974(2)	13.051(3)	28.875(5)
c/Å	36.823(2)	14.308(2)	11.825(2)
α/°		84.345(16)	
β/°	92.428(6)	102.209(10)	
γ/°		88.875(15)	
U/Å^3	17840.7(25)	2113.4(6)	4250.6(11)
Z	16	2	4
D_c/g cm^{-3}	1.749	2.282	2.313
F(000)	9312	1336	2728
μ(Mo-Kα)/cm^{-1}	43.2	86.7	86.3
Crystal colour, shape	Very dark green blocks	Small, dark green, rectangular prisms	Large, deep red prisms
Crystal size/mm	0.36 × 0.26 × 0.24	0.10 × 0.14 × 0.43	0.30 × 0.35 × 0.45
θ_{max}/° for data collection	22.5	23	25
Crystal degradation (% overall)	27.0	18.7	0.0
Transmission factor range	0.85–0.97	0.15–0.23	0.39–0.55
Total no. unique reflections	5823	5868	4181
No. reflections with $I > 2\sigma_I$	3224	4801	3878
No. reflections used in refinement	3589 (with $I > 1.5\sigma_I$)	5478 (with $I > \sigma_I$)	4179 (all but two suspect reflections)
Maximum final shift/e.s.d.	0.63	0.76	0.85
Final R	0.053	0.069	0.040
Weighted R, R_g[36]	0.058	0.107	0.048
Goodness of fit	1.07	0.45	1.30
Reflections weighted, w =	$(\sigma_F^2 + 0.00142F^2)^{-1}$	$(\sigma_F^2 + 0.020F^2)^{-1}$	$(\sigma_F^2 + 0.00081F^2)^{-1}$
Final difference map peaks/e Å^{-3}, location	0.9, *ca.* 1.2 Å from Mo	2.9, *ca.* 1.0 Å from W	1.8, *ca.* 1.1 Å from W

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