

PREPARATION AND CHARACTERIZATION OF $M_2(\text{SeAr}')_6$ AND MIXED LIGAND $M_2(\text{OR})_2(\text{SeAr}')_4$ SPECIES ($M = \text{Mo}, \text{W}$)

MALCOLM H. CHISHOLM,* JOHN C. HUFFMAN, IVAN P. PARKIN
and WILLIAM E. STREIB

Department of Chemistry and Molecular Structure Center, Indiana University,
Bloomington, IN 47405, U.S.A.

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Abstract—Toluene solutions of $M_2(\text{NMe}_2)_6$ ($M = \text{Mo}, \text{W}$) react with mesitylene selenol ($\text{Ar}'\text{SeH}$) to give $M_2(\text{SeAr}')_6$ complexes. $\text{Mo}_2(\text{OR})_6$ ($R = \text{'Bu}, \text{CH}_2\text{'Bu}$) react with excess (> 6 fold) $\text{Ar}'\text{SeH}$ to give $\text{Mo}_2(\text{SeAr}')_6$, whilst $\text{W}_2(\text{OR})_6(\text{py})_2$ ($R = \text{'Pr}, \text{CH}_2\text{'Bu}$) react with excess (> 6 fold) $\text{Ar}'\text{SeH}$ to give $\text{W}_2(\text{OR})_2(\text{SeAr}')_4$. Reaction of $\text{Mo}_2(\text{OPr}^i)_6$ with $\text{Ar}'\text{SeH}$ produces $\text{Mo}_2(\text{OPr}^i)_2(\text{SeAr}')_4$ which crystallizes in two different space groups. These arene-selenato complexes are air-stable and insoluble in common organic solvents. X-ray crystallographic studies revealed that the $\text{Mo}_2(\text{SeAr}')_6$ and $\text{W}_2(\text{SeAr}')_6$ compounds are isostructural in the solid state and adopt ethane-like staggered configurations with the following important structural parameters, $M-M$ ($W-W/\text{Mo}-\text{Mo}$) 2.3000(11)/2.2175(13) Å, $M-\text{Se}$ 2.430 (av.)/2.440 (av.) Å, $M-M-\text{Se}$ 97.0° (av.)°. In the solid state $\text{W}_2(\text{OPr}^i)_2(\text{SeAr}')_4$ adopts the anti-configuration with crystallographically imposed C_i symmetry and $W-W$ 2.3077(7) Å, $W-\text{Se}$ 2.435 (av.) Å, $W-O$ 1.858(6) Å; $W-W-\text{Se}$ 100.27(3)°, 93.8(3)° and $W-W-O$ 108.41(17)°. $\text{Mo}_2(\text{OPr}^i)_2(\text{SeAr}')_4$ crystallizes in both $P\bar{1}$ and $A2/a$ space groups in which the molecules are isostructural with each other and the tungsten analogue. Important bond lengths and angles are $\text{Mo}-\text{Mo}$ 2.180(24) Å, $\text{Mo}-\text{Se}$ 2.432(av.) Å, $\text{Mo}-O$ 1.872(9) Å, $\text{Mo}-\text{Mo}-\text{Se}$ 99.39(9)°, 94.71(8)°, $\text{Mo}-\text{Mo}-O$ 107.55(28)°.

The synthesis of metal-metal multiply bonded compounds has been extensively explored, especially for molybdenum and tungsten.¹ Indeed M_2R_6 ($M = \text{Mo}, \text{W}$) compounds are formed for a range of ligands $R =$ alkoxy, amido, thiolate and various mixed species of general formula $M_2R'_2R_4$, e.g. $M_2\text{Cl}_2(\text{NMe}_2)_4$.²⁻⁴

Previously, there have been a few reports of Cr, Mo and W aryl selenolate complexes.⁵ Two examples which contain μ_2 bridging SePh ligands have been structurally determined by X-ray crystallography,^{6,7} namely, $(\text{C}_7\text{H}_7)\text{Mo}(\mu\text{-SePh})_3\text{Mo}(\text{CO})_3$ and $(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{Cr}(\mu\text{-SePh})_2\text{Cr}(\text{NO})(\eta^5\text{-C}_5\text{H}_5)$. Aryl selenium and tellurium complexes of general formula $[\text{M}(\text{C}_5\text{H}_5)_2(\text{EPh})_2]$ ($M = \text{Ti}, \text{V}, \text{Nb}, \text{Mo}, \text{W}$; $E = \text{S}, \text{Se}, \text{Te}$) have been characterized by elemental analysis and IR spectroscopy and are thought to have terminal aryl-chalcogen ligands.⁸

One tungsten compound containing an aryl-selenolate ligand has been studied by X-ray crystallography, $(\eta^7\text{-C}_7\text{H}_7)\text{W}(\text{CO})_2(\text{SePh})$, and contains a terminal aryl-selenide ligand.⁷

Homoleptic complexes supported by selenolate ligands are known⁹⁻¹⁴ for mercury $[\text{Ph}_4\text{P}][\text{Hg}(\text{SePh})_3]$, lead $[\text{Ph}_4\text{As}][\text{Pb}(\text{SePh})_3]$, tin $[\text{Sn}(\text{SePh})_4]$ and silicon $[(\text{Si}(\text{SePh})_3)_2]$. These species are suggested to have only terminal selenolate ligands. Molybdenum and tungsten compounds of formulation $[\text{OM}(\text{SePh})_4]$ and $[\text{M}_2\text{O}_2(\text{ER})_6\text{OMe}]^-$ ($R = \text{S}, \text{Se}$; $R = \text{aryl}$) have been made and characterized by UV-vis, EPR and elemental analysis.^{14,15} An X-ray crystal structure of the thiolate derivative indicates that the dinuclear species has one bridging μ_2 thiolate group and two μ_2 oxo species, with the remainder of the ligands being terminal.^{16,17} The selenide derivatives of these complexes have inferred structures based upon the thiolato chemistry.

Here we report the synthesis and characteriz-

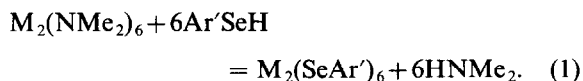
* Author to whom correspondence should be addressed.

ation of homoleptic molybdenum and tungsten multiply bonded compounds supported by mesitylene selenol ligands. The choice of the mesityl group was influenced by considerations of steric bulk and C—S bond cleavage.^{3,4} The preparations of $M_2(OR)_2(SeAr')_4$ ($M = Mo, W$) are also presented. To our knowledge these are the first examples of homoleptic transition metal selenolate complexes.^{5,18}

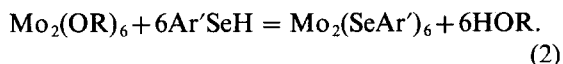
RESULTS AND DISCUSSION

Syntheses and characterization

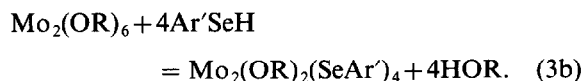
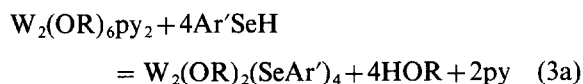
$M_2(SeAr')_6$ and $M_2(SeAr')_4(OR)_2$ compounds. All the reactions were performed at room temperature in toluene or toluene–hexane mixtures. Reaction of $M_2(NMe_2)_6$ ($M = Mo, W$) with excess (> 6 fold) $Ar'SeH$ produced the completely substituted $M_2(SeAr')_6$ complex, eq. (2) (N.B. Ar' , here and after is used for the mesitylene ligand; 2,4,6-trimethyl benzene):



$Mo_2(OR)_6$ ($R = 'Bu, CH_2'Bu$) also reacts with $Ar'SeH$ to give complete substitution, eq. (2). The alcohol generated can be detected in the 1H NMR spectra of the filtrate:



Surprisingly, reaction of $W_2(OR)_6 \cdot py_2$ ($R = CH_2'Bu, 'Pr$), $W_2(O'Bu)_6$ or $Mo_2(OR)_6$ ($R = 'Pr, 'Hex$) with excess (> 6 fold) of mesitylene selenol does not produce the fully substituted species, but rather the tetrasubstituted species $M_2(OR)_2(SeAr')_4$, eq. (3):



The reason for the complete substitution in the amide case for both Mo and W [eq. (1)], when compared to the analogous sulphur chemistry is not obvious.³ One explanation could be the complete insolubility of the products in eq. (3) in common organic solvents, thus providing a driving force for the reaction.

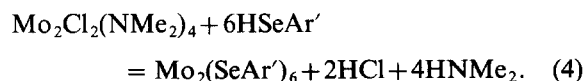
The reaction of $M_2(OR)_6$ with a six-fold excess of mesitylene selenol leads to complete substitution at room temperature in the case of some molybdenum compounds ($OR = 'Bu, CH_2'Bu$) but

stops at the tetrasubstituted tungsten species. The complete substitution at room temperature in the molybdenum case ($OR = 'Bu, CH_2'Bu$) is surprising in the light of the corresponding thiolate chemistry where forcing conditions ($80^\circ C$) are required. Possibly the larger covalent radius of selenium compared with sulphur ($0.09 \text{ \AA}$) is sufficient to alter the relative reactivity of the intermediate $M_2(EAr')_x(OR)_{6-x}$ ($x = 1-5$) compounds ($E = S, Se$). The increased acidity of a selenol compared with a thiol would also facilitate the generation of the selenolate.

In general, the reaction to form the $Mo_2(SeAr')_6$ species occurs faster for amide [eq. (1)] than alkoxide replacement [eq. (2)]. The rate of reaction (as judged by the rate of product precipitation) is dependent on the bulk of the alkoxide with the $O'Bu$ derivative requiring less time for reaction than the $OCH_2'Bu$ derivative [eq. (2)]. This indicates a degree of steric control in the reaction. The tungsten reaction to form $W_2(OR)_2(SeAr')_4$ is much slower than the reaction to form the fully substituted molybdenum species. At room temperature little reaction occurs between $W_2(O'Bu)_6$ and mesitylene selenol after 6 days in hydrocarbon solvents. However a reaction time of 2 weeks in THF followed by cooling to $-20^\circ C$ for 30 days allowed isolation of $W_2(O'Bu)_2(SeAr')_4$.

Reaction of $Mo_2(OR)_6$ ($R = 'Bu, CH_2'Bu$) with $Ar'SeH$ goes to complete substitution and formation of $Mo_2(SeAr')_6$ [eq. (2)], whilst for $R = 'Pr$ and cyclohexyl ($'Hex$), the tetrasubstituted species $Mo_2(SeAr')_4(OR)_2$ are formed. This is probably due to the solubility of the tetrasubstituted derivative. For $R = 'Pr$ and $'Hex$ the tetrasubstituted species are very insoluble, whilst a purported $Mo_2(SeAr')_4(OR)_2$ ($R = 'Bu, CH_2'Bu$) species would be expected to be more soluble (based on the relative solubilities of $Mo_2(O'Bu)_6$, $Mo_2(OCH_2'Bu)_6$ and $Mo_2(O'Hex)_6$ in hydrocarbon solvents).

Treatment of a solution of $Mo_2Cl_2(NMe_2)_4$ in toluene with excess mesitylene selenol also leads to $Mo_2(SeAr')_6$ formation, eq. (4). The yields of the product are comparable to those obtained by the other routes, although the microanalysis is slightly inferior.



The $M_2(SeAr')_6$ and $M_2(OR)_2(SeAr')_4$ ($M = Mo, W$) compounds were characterized by IR spectroscopy, melting points and X-ray crystallography. Unfortunately, the insolubility precluded an NMR study of the $M_2(SeAr')_6$ product. However,

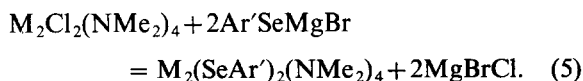
the mixed alkoxide/selenolate species $M_2(\text{OR})_2(\text{SeAr}')_4$ are slightly soluble in THF, chloroform or toluene to about 15 mg in 100 cm³ of solvent.

The homoleptic compounds $M_2(\text{SeAr}')_6$ are relatively air-stable and show little detectable physical changes (IR/m.p./colour) even when stored in the light over 5 months. They are insoluble in and show no decomposition by water. Addition of 6 M HNO_3 to the hexaselenolates causes slow decomposition but requires a long time for reaction due to the high crystallinity of the sample. These physical properties are probably attributable to the hydrophobic exterior presented by the mesitylene ligands.

The IR spectra of the hexaselenolates exhibit the expected ligand vibrations due to coordinated mesitylene selenol and a stretch at low frequency at *ca* 285 or 260 cm⁻¹ (in the molybdenum and tungsten cases, respectively), which can be assigned to M—Se vibrations. The mixed $M_2(\text{SeAr}')_4(\text{OR})_2$ species exhibit vibrations due to both the selenolate and alkoxide ligands.

The ¹H NMR spectra of $M_2(\text{SeAr}')_4(\text{OR})_2$ (M = Mo, R = Prⁱ, cyclohexyl; M = W, R = Prⁱ, Buⁱ, neopentyl) measured at room temperature show the expected resonances for both the selenolate and alkoxide ligands in the correct integral ratios and are consistent with the anti-rotamer. The spectra required a long accumulation time because of the low solubility of the materials.

$M_2(\text{SeAr}')_2(\text{NMe}_2)_4$. The reaction between $M_2\text{Cl}_2(\text{NMe}_2)_4$ and mesitylene selenium Grignard $\text{Ar}'\text{SeMgBr}$ in THF leads to the precipitation of yellow crystals, $M_2(\text{SeAr}')_2(\text{NMe}_2)_4$ in a 40% yield based on eq. (5). These compounds are slightly soluble in THF–toluene and chloroform, and are air and light sensitive, especially in solution. The ¹H NMR spectrum of $M_2(\text{SeAr}')_2(\text{NMe}_2)_4$ in benzene reveals only the anti-rotamer. The corresponding thiolate $\text{Mo}_2(\text{SAr}')_2(\text{NMe}_2)_4$ adopts an ethane staggered geometry about the metal–metal triple bond with the aryl thiolato ligands in an anti-configuration in the solid state. Attempts to obtain an X-ray determination of the selenolate derivative were hampered by problems of twinning. The IR spectra of $M_2(\text{SeAr}')_2(\text{NMe}_2)_4$ have bands directly assignable to the amide and coordinated selenolate ligands.



Attempted preparations of phenylselenolates. The reactions between $M_2(\text{NMe}_2)_6$ or $M_2(\text{OR})_6 \cdot L_2$ (M = Mo, W, L = py, HNMe_2) and selenophenol (HSePh) at room temperature in hydrocarbon solvents produce a purple precipitate for molybdenum

and a black solid for tungsten. The reactions with $M_2(\text{NMe}_2)_6$ produce ammonium salts as evidenced by the IR spectra of both the molybdenum and tungsten products. In the molybdenum case the reaction is extremely rapid and the product formulated as having an empirical formula $[\text{Mo}_4(\text{SePh})_{10}\text{Se}_2]\text{H}_2\text{NMe}_2$ on the basis of microanalysis and IR spectroscopy. The latter showed vibrations associated with the selenophenol ligand as well as the Me_2NH_2^+ ion at 2700 and 2400 cm⁻¹ ($\bar{\nu}$ NH) for the complex.¹⁸ The product is also air-stable (no change in IR spectrum over 1 month at room temperature in air) and insoluble in organic solvents. The reaction between $\text{Mo}_2(\text{O}^i\text{Bu})_6$ and phenylselenol also produces a purple solid which has a very similar IR to $[\text{Mo}_4(\text{SePh})_{10}\text{Se}_2]\text{H}_2\text{NMe}_2$, but missing the vibrations associated with the Me_2NH_2^+ ion. However, new bands at 3200 and 1630 cm⁻¹, as well as O^iBu vibrations suggest hydrogen bonding involving $[\text{H}_2\text{O}^i\text{Bu}]^+$.

The reaction between $W_2(\text{NMe}_2)_6$ and selenophenol proceeded in an analogous manner to the molybdenum compounds and produced a black solid, the microanalysis and IR of which are consistent with the empirical formula $[\text{W}_4\text{Se}_4(\text{SePh})_{10}]\text{H}_2\text{NMe}_2$. This material is insoluble in common solvents once isolated. If the reaction to form this material is performed in THF the tungsten species is not precipitated until after 2 days, compared with 3 h for reactions in hydrocarbon solvents.

The solubility of the compounds produced in the reaction of non-sterically protected selenophenols with tungsten and molybdenum amides and alkoxides was not improved by the use of *para*-substituted selenophenols such as *p*- $\text{EtOC}_6\text{H}_4\text{—SeH}$.

Solid state structures of $M_2(\text{SeAr}')_6$ (M = Mo, W)

Crystal data for the $M_2(\text{SeAr}')_6$ compounds are given in Table 1; selected bond lengths and angles in Table 2. An ORTEP view of the molecule showing the atom numbering scheme used in the tables is shown in Fig. 1 for $W_2(\text{SeC}_6\text{H}_2\text{Me}_3)_6$, and a view down the Mo—Mo axis in $\text{Mo}_2(\text{SeC}_6\text{H}_2\text{Me}_3)_6$ is given in Fig. 2.

The sample of $W_2(\text{SeAr}')_6$ that was examined crystallographically, crystallized from the reaction involving $W_2(\text{NMe}_2)_6$ and $\text{Ar}'\text{SeH}$ on standing at room temperature for 4 days. No included solvent was present and the compound formed with a crystallographically imposed centre of symmetry in the space group $P\bar{1}$.

The sample of $\text{Mo}_2(\text{SeC}_6\text{H}_2\text{Me}_3)_6$ used for X-ray analysis, crystallized from the reaction solution involving $\text{Mo}_2(\text{O}^i\text{Bu})_6$ with excess mesitylene

Table 1. Summary of crystal data

	I	II	III	IV	V
Empirical formula	$W_2C_{54}H_{66}Se_6$	$Mo_2C_{54}H_{66}Se_6$	$W_2C_{42}H_{58}O_2Se_4$	$Mo_2C_{42}H_{58}Se_4O_2$	$Mo_2C_{42}H_{58}Se_4O_2$
Colour of crystal	Brown	Red	Red	Yellow	Red-Orange
Crystal dimensions (mm)	$0.14 \times 0.16 \times 0.28$	$0.25 \times 0.25 \times 0.25$	$0.30 \times 0.30 \times 0.16$	$0.25 \times 0.25 \times 0.25$	$0.08 \times 0.10 \times 0.52$
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$A2/a$
Cell dimensions					
Temperature ($^{\circ}C$)					
a (Å)	11.727(4)	11.747(2)	10.805(1)	10.846(2)	10.846(2)
b (Å)	11.765(3)	11.725(2)	11.434(1)	11.355(2)	11.355(2)
c (Å)	11.158(3)	11.139(2)	9.428(1)	9.396(1)	9.396(1)
α ($^{\circ}$)	95.66(1)	95.49(1)	98.28(1)	98.68(1)	98.68(1)
β ($^{\circ}$)	95.93(2)	96.11(1)	110.62(1)	110.57(1)	110.57(1)
γ ($^{\circ}$)	118.27(2)	118.20(1)	88.75(1)	88.51(1)	88.51(1)
Z (molecules/cell)	1	1	1	1	4
Volume (Å ³)	1329.32	1325.59	1078.26	1070.63	1070.63
Calculated density (g cm ⁻³)	1.944	1.730	1.969	1.710	1.613
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069	0.71069
Molecular weight	1556.58	1380.76	1278.46	1102.64	1102.64
Linear absorption coefficient (cm ⁻¹)	85.178	45.741	88.206	39.710	37.920
Detector to sample distance (cm)	22.5	22.5	22.5	22.5	22.5
Sample to source distance (cm)	23.5	23.5	23.5	23.5	23.5
Average Ω scan width at half-height	0.25	0.25	0.25	0.25	0.25
Scan speed ($^{\circ}$ min ⁻¹)	8.0	8.0	8.0	4.0	4.0
Scan width (+dispersion)	2.0	2.0	2.0	2.0	2.0
Individual background (s)	3	3	4	6	8
Aperture size (mm)	3.0×4.0	3.0×4.0	3.0×4.0	3.0×4.0	3.0×4.0
2θ Range ($^{\circ}$)	6-45	6-45	6-45	6-45	6-45
Total number of reflections collected	3552	4398	3023	3369	6447
Number of unique intensities	3480	3467	2834	2797	2938
Number with $F > 0.0$	3306	3256	2758	2603	2582
Number with $F > 2.33\sigma(F)$	3142	2936		2415	2302
Number with $F > 3*\sigma(F)$			2417		
$R(F)$	0.0443	0.0417	0.0330	0.056	0.0703
$R_w(F)$	0.0436	0.0415	0.0357	0.0559	0.0634
Goodness of fit for the last cycle	1.424	1.037	1.910	1.415	1.515
Maximum δ/σ for the last cycle	0.18	0.12	0.049	0.05	0.35

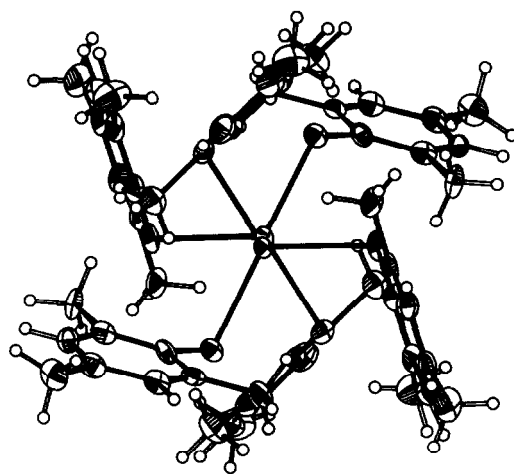
Table 2. Selected bond distances (Å) and angles (°) for the $M_2(\text{SeC}_6\text{H}_2\text{Me}_3)_6$ molecules

A	B	Distance	
		W	Mo
M(1)	M(1)'	2.3000(11)	2.2175(13)
M(1)	Se(2)	2.4214(15)	2.4324(11)
M(1)	Se(3)	2.4278(14)	2.4385(11)
M(1)	Se(4)	2.4457(16)	2.4568(12)
Se(2)	C(5)	1.951(11)	1.938(7)
Se(3)	C(14)	1.956(11)	1.956(7)
Se(4)	C(23)	1.957(11)	1.956(7)

A	B	C	Angle	
			W	Mo
M(1)	M(1)'	Se(2)	96.46(5)	96.56(5)
M(1)	M(1)'	Se(3)	96.92(4)	97.18(5)
M(1)	M(1)'	Se(4)	97.68(5)	98.17(5)
Se(2)	M(1)	Se(3)	116.91(5)	116.70(4)
Se(2)	M(1)	Se(4)	120.13(5)	120.04(4)
Se(3)	M(1)	Se(4)	118.54(5)	118.48(4)
M(1)	Se(2)	C(5)	104.3(3)	104.64(22)
M(1)	Se(3)	C(14)	106.1(3)	106.57(22)
M(1)	Se(4)	C(23)	105.6(3)	105.82(21)

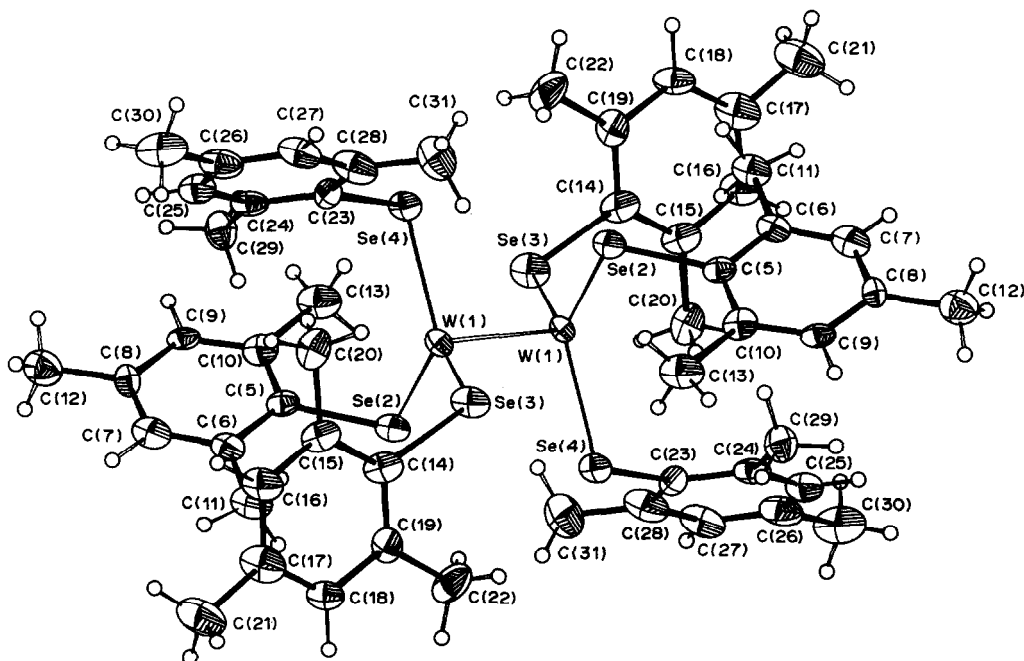
selenol in toluene at room temperature overnight. The molybdenum compound was isostructural with the tungsten analogue.

A comparison of the parameters associated with the central $X_3M\equiv MX_3$ core in structurally char-

Fig. 2. ORTEP view down the Mo—Mo axis in $\text{Mo}_2(\text{SeAr}')_6$.

acterized homoleptic alkyls, amides, alkoxides and thiolates has been made previously.⁴ For related molecules the W—W distance is longer by *ca* 0.08 Å than the Mo—Mo distances.^{3,4} This difference is found in the $M_2(\text{SeAr}')_6$ compounds.

The M—Se distance in $M_2(\text{SeAr}')_6$ is (within the 3 σ criteria) the same for Mo and W, 2.43(av.) Å. This M—Se distance is significantly shorter than that observed in the mononuclear $(\eta^7\text{-C}_7\text{H}_7)\text{W}(\text{CO})_2\text{SePh}$ complex, 2.588(2) Å, and the dimeric $(\text{C}_6\text{H}_7)\text{Mo}(\mu\text{-SePh})_3\text{Mo}(\text{CO})_3$ complex, *ca* 2.56 (av.) Å.^{6,7} The metal-selenium bond lengths are also shorter than that in the "diselenide complex" $[\text{W}_2(\text{CO})_{10}\text{Se}_4][\text{SbF}_4]_2$, 2.626(2) and 2.631(2) Å,

Fig. 1. ORTEP view of $\text{W}_2(\text{SeAr}')_6$.

respectively.¹⁶ Although these distances are not directly comparable due to differing electronic and steric effects produced by different sets of ligands, the relative shortness of the M—Se bonds in the $M_2(SeAr)_6$ complexes is suggestive of metal–selenium π -bonding. The presence of the methyl groups on the mesitylene ligand probably help to stop bridge formation in the $M_2(SeAr)_6$ complexes.

The M—M—X angles in $M_2(SeAr')_6$ span a small range 96.4–98.2°, and are essentially the same for both the tungsten and molybdenum complexes. These angles are more acute than those in the homoleptic alkyl, amide or alkoxide M_2R_6 complexes, where 100–103° is the normal.¹ The thiolate $M_2(SAr')_6$ complexes⁴ have M—M—X angles of comparable magnitude to the selenolate complexes; Mo—Mo—S = 96.6(2)°, W—W—S = 97.4(av.)°. The smaller angles for the selenates and thiolates can be explained in terms of the arrangement of all six mesityl groups, which are distal with respect to the central M—M core. In a typical alkoxide case, e.g. $Mo_2(OCH_2Bu^t)_6$,¹ four groups are distal and two are proximal generating larger and smaller M—M—X angles, with the average angle being larger than the thiolate or selenolate case.

The Mo—Mo distance in $Mo_2(SeAr')_6$ of 2.2176(13) Å is typical of those found in $(Mo\equiv Mo)^{6+}$ containing compounds ($d = 2.15$ – 2.23 Å) and slightly shorter than the corresponding $Mo_2(SAr')_6$ complex at 2.228(1) Å. The W—W bond in $W_2(SeAr')_6$ is also typical of a $(W\equiv W)^{6+}$ moiety at 2.300 Å, and is further significantly shorter (0.012 Å) than the corresponding thiolate analogue.⁴

The M—Se distances are longer (by 0.11 Å) in

$M_2(SeAr')_6$ than the M—S bond lengths in $M_2(SAr')_6$ complexes. This is not surprising as selenium has a larger covalent radius than sulphur (1.11 Å compared with 1.02 Å). For the $M_2(SAr')_6$ molecules a case of substantial M—S π -bonding has been forwarded on the basis of the short Mo—S distances observed when compared with the relevant covalent radii.³ The case for selenium to metal π -bonding can be similarly made, especially since sulphur and selenium have the same electronegativities on the Pauling scale.²⁰ In general, the covalent radius of selenium is 0.09 Å greater than for sulphur in analogous compounds. The M—S distances in the thiolate analogues $M_2(SAr')_6$ are 0.15 Å shorter than those expected on the basis of covalent radii. This has led to the suggestion of substantial π character in the metal to sulphur bond.^{3,4} In the $M_2(SeAr')_6$ species, the M—Se bond lengths are 0.11 Å longer than the sulphur analogue. This indicates that there is a contraction of 0.13 Å in the M—Se bond lengths $[0.15 + 0.09 - 0.11]$ in the homoleptic species that may be attributable to the existence of Se-to-M π -bonding. Other reported M—Se bond lengths include 2.512(3) Å in $Sn(SePh)_4$ and 2.727(1) Å in $[Ph_4As][Pb(SePh)_3]$.^{11,12}

$M_2(SeAr')_4(O^iPr)_2$

Crystal data for the $M_2(SeAr')_4(O^iPr)_2$ molecules are given in Table 1; selected bond lengths and angles in Table 3. An ORTEP view of the tungsten derivative showing the atom numbering scheme used in the tables is given in Fig. 3, and a stereo-

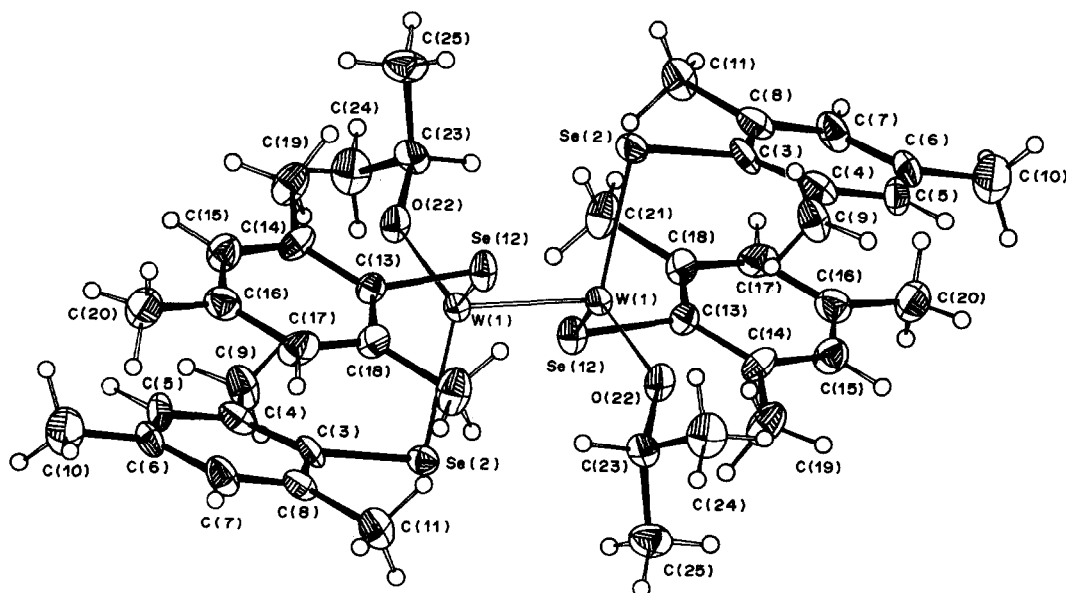


Fig. 3. ORTEP view of $W_2(SeAr')_4(O^iPr)_2$.

Table 3. Selected bond distances (Å) and bond angles (°) for $\text{Mo}_2(\text{SeC}_6\text{H}_2\text{Me}_3)_4(\text{O}^i\text{Pr})_2$ molecules

A	B	Distance		
		W	Mo ^a	Mo' ^b
M(1)	M(1)'	2.3077(7)	2.2192(17)	2.2180(24)
M(1)	Se(2)	2.4303(10)	2.4353(14)	2.4281(21)
M(1)	Se(12)	2.4410(10)	2.4476(14)	2.4427(19)
M(1)	O(22)	1.858(6)	1.873(6)	1.872(9)
Se(2)	C(3)	1.955(9)	1.938(10)	1.954(13)
Se(12)	C(13)	1.959(9)	1.955(9)	1.947(13)
O(22)	C(23)	1.449(10)	1.435(11)	1.441(16)

A	B	C	Angle		
			W	Mo ^a	Mo' ^b
M(1)'	M(1)	Se(2)	100.27(3)	100.17(6)	99.39(9)
M(1)'	M(1)	Se(12)	93.85(3)	94.04(5)	94.71(8)
M(1)'	M(1)	O(22)	108.41(17)	108.55(20)	107.55(28)
Se(2)	M(1)	Se(12)	120.14(3)	119.73(5)	118.59(7)
Se(2)	M(1)	O(22)	111.32(18)	112.68(21)	113.8(3)
Se(12)	M(1)	O(22)	118.43(18)	117.28(2)	117.9(3)
W(1)	Se(2)	C(3)	90.07(25)	89.9(3)	94.6(4)
W(1)	Se(12)	C(13)	107.72(25)	106.7(3)	106.0(4)
W(1)	O(22)	C(23)	140.5(5)	139.8(6)	140.2(8)
Se(2)	C(3)	C(4)	121.2(6)	120.8(7)	119.0(10)
Se(2)	C(3)	C(8)	118.5(6)	120.1(7)	119.0(10)

^a Yellow plates.^b Orange-red needles.

view of the molecule looking down the Mo—Mo bond axis is given in Fig. 4.

The crystal used for X-ray analysis crystallized from the reaction solution of $\text{W}_2(\text{OPr}^i)_6(\text{py})_2$ with excess ArSeH on standing at room temperature. The molecule has a crystallographically imposed centre of inversion in the space group $P\bar{1}$. The mesityl and isopropyl groups are with respect to the W—W bond distal and proximal, respectively, and the structure is very similar to that adopted by $\text{Mo}_2(\text{OPr}^i)_2(\text{SAr})_4$.

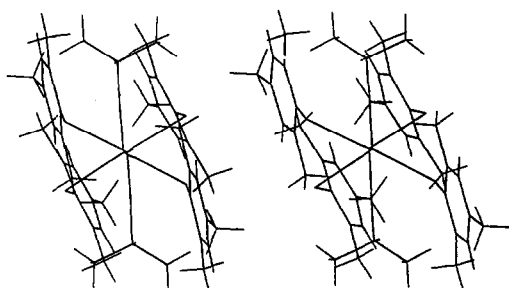


Fig. 4. Stereo-view of $\text{Mo}_2(\text{SeAr}')_4(\text{OPr}^i)_2$ down the Mo—Mo axis.

The crystals of $\text{Mo}_2(\text{SeAr}')_4(\text{O}^i\text{Pr})_2$ used for the analysis are crystallized out of the reaction solution of $\text{Mo}_2(\text{O}^i\text{Pr})_6$ with excess (> 6-fold) mesitylene selenol, on cooling the reaction to -20°C after 10 days at room temperature. Two types of crystals were observed from the reaction mixture, yellow plates (10%) and red-orange needles (90%). Both samples were examined crystallographically and found to be $\text{Mo}_2(\text{SeAr}')_4(\text{O}^i\text{Pr})_2$. The molecules have a centre of symmetry and were found to be isostructural with each other and the tungsten species $\text{W}_2(\text{SeAr}')_4(\text{O}^i\text{Pr})_2$.

The W—W distance of 2.3077(7) Å in $\text{W}_2(\text{SeAr}')_4(\text{O}^i\text{Pr})_2$ is typical of a W—W triple bond although slightly longer than the bond length observed in $\text{W}_2(\text{SeAr}')_6$. The W—Se bond lengths are comparable within the 3σ criteria to those observed in the homoleptic compound. The W—O bond lengths at 1.858(6) Å are slightly shorter than those normally observed in multiple bonded tungsten compounds supported by alkoxide ligands (ca 1.94–1.89(av.) Å).¹ This difference is not considered significant as it is comparable to the difference between the bond lengths in $\text{Mo}_2(\text{OCH}_2^i\text{Bu})_6$.^{1,21}

Thus, the substitution of four alkoxy groups by four areneselenolate ligands has little overall effect on the RO-to-M bonding. As was observed for the homoleptic compounds the W—Se and Mo—Se bond lengths are shorter than expected on the basis of covalent radii, suggestive of Se-to-M π -bonding.

The W—W—O angle at 108.41(17) is close to those observed for other alkoxides. The two W—W—Se angles are significantly different at 93.85(3) and 100.27(3)°, respectively. This pattern was observed for the similar compound Mo₂(OⁱPr)₂(SAr')₄ which had angles of 95.4(0) and 99.8(0)°.⁴

The Mo—Mo bond distances 2.2192(17) and 2.2180(24) Å in Mo₂(SeAr')₄(OⁱPr)₂ are normal for triple bonds between molybdenum atoms and equivalent to that in Mo₂(SeAr')₆. The other bond lengths and bond angles are essentially the same as those in the tungsten analogue W₂(SeAr')₄(OⁱPr)₂.

EXPERIMENTAL

All reactions were performed under a nitrogen atmosphere in degassed and distilled solvents. The preparation of M₂(NMe₂)₆ (M = Mo, W), M₂(OR)₆ (M = Mo, W; R = CH₂ⁱBu)₃, ⁱBu, ⁱPr, ^cHex and W₂(OR)₆(py)₂ (R = ⁱPr, CH₂ⁱBu; L = py, HNMe₂) were as previously described.^{21–24} Phenyllithium, mesitylene magnesium bromide and selenium metal were purchased from Aldrich Chemical Co. Mesitylene selenol was prepared from the reaction of mesityl Grignard and elemental selenium as described below. ¹H NMR spectra were obtained in *d*⁸-THF, CDCl₃ or C₆D₆ on a Nicolet 360 spectrometer operating at 360.12 MHz and referenced to internal residual protio THF, chloroform and benzene at 1.73, 7.24 and 7.15 ppm, respectively. Mass spectra were obtained on a Kratos MS450. IR spectra were recorded either as KBr discs or Nujol mulls using a Perkin–Elmer 283 spectrophotometer. Elemental analyses were obtained from Oneida Research Services (Whiteborough, New York).

Mesitylene Selenol

To a solution of mesitylene magnesium bromide (50 cm³ of 1 M solution in THF) was added over 1 h with stirring grey selenium powder (4.0 g, 50 mmol). The solution was stirred overnight at room temperature with all the selenium dissolving to produce a light-green solution. The solution was hydrolysed by the cautious dropwise addition of water (20 cm³) followed by 20 cm³ of 6 N HCl. The upper orange THF layer was collected and dried over

anhydrous MgSO₄ for 24 h. After filtration from the MgSO₄ the THF was removed *in vacuo* to leave a yellow oil (6.8 g, 34.4 mmol, 69%) which was purified by distillation (*ca* 55°C, 1.10^{–4} torr). MS: M⁺ = 199; ¹H NMR (C₆H₆): δ = 6.67 (s, 2H), 2.18 (s, 6H), 2.04 (s, 3H). IR (KBr plates): 3000br, 2930s, 2900s, 2850sh, 2300w, 1540m, 1435s, 1370m, 1350w, 1270w, 1025s, 870w, 840s, 680s, 540s, 340m cm^{–1}. (Introduction of air helps to provide formation of mesitylene diselenide which crystallizes from the oil on standing.) (C₆H₂Me₃Se)₂; MS: M⁺ = 396, ¹H NMR: δ = 6.69 (s, 4H), 2.31 (s, 12H), 2.03 (s, 6H).

Phenyl Selenol

To a solution of phenyllithium (25 cm³, 1.8 M solution in cyclohexane–diethyl-ether 80:20) was added THF (5 cm³) and powdered grey selenium (3.55 g, 0.045 mol). The reaction was stirred for 18 h at room temperature with all the selenium dissolving to give a light-green solution. The solution was hydrolysed by the cautious dropwise addition of water (15 cm³) (very exothermic reaction), followed by 6 N HCl (15 cm³). The upper orange layer was decanted and dried over anhydrous MgSO₄. Removal of the solvent under vacuum gave selenophenol (4.42 g, 0.27 mmol, 60%), which was purified by distillation at 57°C/8 torr.

[*Caution*: Phenyl and mesitylene selenol are very malodorous and all operations should be performed in a well ventilated hood. The glassware is best cleaned after the reaction by soaking in sodium hypochlorite (4% solution) for 1 day, decanting off the liquid then adding to a KOH–EtOH bath.]

W₂(SeAr')₆

W₂(NMe₂)₆ (0.100 g, 0.158 mmol) was dissolved in toluene (20 cm³) at room temperature. Mesitylene selenol (0.250 g, 1.25 mmol) was added dropwise to the stirred solution causing an immediate darkening in colour from yellow to red. The stirring was continued for 5 min then the solution allowed to stand at ambient temperature for 3 days, during which time dark-red–brown crystals of W₂(SeAr')₆ (0.154 g, 0.0985 mmol, 62.3%) formed. These were collected by filtration, washed with hexane (20 cm³) and THF (20 cm³) and air dried. Found: C, 41.7; H, 4.3; N, 0.0. Calc.: C, 42.2; H, 4.2%. IR (KBr disc): 3000m, 2945m, 2895m, 1585w, 1552w, 1520w, 1442vs, 1420vs, 1360m, 1290s, 1161w, 1080w, 1015sh, 1002vs, 940w, 866w, 835vs, 716w, 690w, 554w, 535m, 455w, 400w, 325sh, 315m, 245s cm^{–1}. M.p. = 162–164°C, decomp. These crystals were suitable for X-ray analysis as described below.

$\text{Mo}_2(\text{SeAr}')_6$

Mesitylene selenol (0.40 g, 2.01 mmol) was dissolved in toluene–hexane (10:10 cm^3) and stirred for 0.5 h at room temperature. Solid $\text{Mo}_2(\text{NMe}_2)_6$ (0.100 g, 0.122 mmol) was added to produce an immediate colour change in the solution to dark-red and after 10 min with stirring, to dark-brown with a red precipitate. The mixture was stirred overnight and the solid collected by filtration and washed with hexane (20 cm^3), THF (30 cm^3), toluene (20 cm^3) and diethyl-ether (20 cm^3); $\text{Mo}_2(\text{SeAr}')_6$ (0.186 g, 0.134 mmol, 61%). IR (KBr disc): 3000w, 2960m, 2900m, 2840m, 1708w, 1588w, 1552w, 1535w, 1520w, 1442vs, 1430vs, 1390sh, 1368s, 1290s, 1162m, 1080w, 1016s, 1002vs, 940m, 865m, 838vs, 716m, 690s, 556m, 540s, 460w, 410w, 331m, 320sh, 285vs cm^{-1} . M.p. 168–172°C, decomp. Found: C, 46.9; H, 4.7; N, 0.0. Calc. for $\text{Mo}_2(\text{SeAr}')_6$: C, 47.0; H, 4.8%.

Alternative procedure 1. To a solution of $\text{Mo}_2(\text{OBu}^t)_6$ (0.100 g, 0.159 mmol) in toluene (20 cm^3) at room temperature was added excess mesitylene selenol (0.25 g, 1.26 mmol). The solution was stirred for 5 min, causing an intense dark-red colour. This was allowed to stand at room temperature for 5 days to produce dark-red crystals of $\text{Mo}_2(\text{SeC}_6\text{H}_2(\text{CH}_3)_3)_6$ (0.148 g, 0.107 mmol, 67%). Found: C, 47.7; H, 4.8; N, 0.0. Calc.: C, 47.0; H, 4.8%. IR and melting points were identical to the compounds made above. The crystals were of X-ray quality and the structure was determined as outlined above.

The reaction can also be repeated with the same procedure, reaction scale and conditions, but using $\text{Mo}_2(\text{OCH}_2^t\text{Bu})_6$ instead of $\text{Mo}_2(\text{OBu}^t)_6$ to give $\text{Mo}_2(\text{SeAr}')_6$ (0.095 g, 0.068 mmol, 43%).

Alternative procedure 2. To a solution of $\text{Mo}_2\text{Cl}_2(\text{NMe}_2)_4$ (0.035 g, 0.08 mmol) in toluene (35 cm^3) at room temperature was added mesitylene selenol (0.20 g, 1.00 mmol) to generate a dark-red coloured solution. The solution was stirred for 5 min and then left to stand overnight (10 h) to produce brown–red crystals. The crystals were filtered and washed with THF (10 cm^3), ethanol (15 cm^3), toluene (15 cm^3) and diethyl-ether (10 cm^3); $\text{Mo}_2(\text{SeAr}')_6$ (0.035 g, 0.025 mmol, 33%). Found: C, 47.5; H, 4.7; N, 0.10. Calc.: C, 47.0; H, 4.8%.

 $\text{W}_2(\text{SeAr}')_4(\text{O}^i\text{Pr})_2$

Solid $\text{W}_2(\text{OPr}^i)_6(\text{py})_2$ (0.100 g, 0.114 mmol) was added to a stirred solution of mesitylene selenol (0.40 g, 2.0 mmol) in toluene (20 cm^3) at room temperature generating a dark-red solution. The solution was stirred by a magnetic follower for 10

min and then allowed to stand for 3 days at room temperature. This produced red crystals of $\text{W}_2(\text{SeAr}')_4(\text{O}^i\text{Pr})_2$ (0.068 g, 0.077 mmol, 67%) which were collected by filtration and washed with pentane (20 cm^3) and THF (20 cm^3). Found: C, 39.5; H, 4.5; N, 0.0. Calc.: C, 39.4; H, 4.5%. IR (KBr disc): 3000w, 2945m, 2895m, 2845sh, 1580w, 1560w, 1430vs, 1410s, 1380sh, 1362m, 1350m, 1310m, 1380m, 1150m, 1090s, 1005s, 960vs, 845m, 832s, 710m, 695w, 600m, 550w, 530w, 460m, 440m cm^{-1} . M.p. 135°C darkens, does not melt below 360°C. ^1H NMR at 22°C in CDCl_3 : δ = 6.85 (s, 8H), 4.03 (br, 2H), 2.35 (s, 24H), 2.24 (s, 12H), 1.28 (s, 12H).

 $\text{W}_2(\text{SeAr}')_4(\text{OCH}_2^t\text{Bu})_2$

Solid $\text{W}_2(\text{OCH}_2^t\text{Bu})_6(\text{py})_2$ (0.091 mg, 0.087 mmol) was added to a stirred solution of mesitylene selenol (0.20 g, 1.00 mmol) in toluene (20 cm^3) at room temperature to form a dark-red solution. The solution was allowed to stand at room temperature for 8 days and then cooled to -20°C for 3 days to produce red crystals of $\text{W}_2(\text{SeAr}')_4(\text{OCH}_2^t\text{Bu})_2$ (0.040 g, 0.29 mmol, 33%). IR (KBr disc): 3000w, 2940s, 2900m, 2840s, 1455s, 1435m, 1385m, 1365m, 1355m, 1285m, 1170w, 1030vs, 940w, 930w, 860w, 840s, 745w, 725m, 685vs, 605w, 605w, 550w, 535w, 460w, 445w, 410w, 390w, 310w, 270w cm^{-1} . ^1H NMR at 22°C (CDCl_3): δ = 6.85 (s, 8H), 3.33 (s, 4H), 2.31 (s, 24H), 2.24 (s, 12H), 0.84 (s, 18H).

 $\text{W}(\text{O}^t\text{Bu})_2(\text{SeAr}')_4$

Mesitylene selenol (0.20 g, 1.0 mmol) was added dropwise to a stirred solution of $\text{W}_2(\text{O}^t\text{Bu})_6$ (0.050 g, 0.062 mmol) in THF (10 cm^3) at room temperature. This caused an immediate darkening of the solution to dark red. The mixture was allowed to stand at room temperature for 2 weeks and then cooled to -20°C for 30 days. This produced lustrous red crystals of $\text{W}_2(\text{O}^t\text{Bu})_2(\text{SeAr}')_4$ which were obtained by decanting the solution and washing with hexane (5 cm^3), toluene (5 cm^3) and THF (5 cm^3) (0.021 g, 0.016 mmol, 26%). ^1H NMR at 26°C (C_6D_6): δ = 6.68 (s, 8H), 2.182 (s, 24H), 2.042 (s, 12H), 1.036 (s, 18H). IR (KBr disc): 2958s, 2900sh, 1450s, 1365m, 1351m, 1288w, 1225m, 1150s, 1010s, 960vs, 900w, 835s, 690w, 600w, 540s, 460s, 410s, 390s, 315w, 270s cm^{-1} . Found: C, 40.6; H, 4.4; N, 0.0. Calc.: C, 40.5; H, 4.7%.

 $\text{Mo}_2(\text{SeAr}')_4(\text{O}^c\text{Hex})_2$

Mesitylene selenol (0.20 g, 1.00 mmol) was added dropwise with stirring to a slurry of $\text{Mo}_2(\text{O}^c\text{Hex})_6$ (0.05 g, 0.064 mmol) in toluene (20 cm^3). The solu-

tion turned dark red, and after 10 min with stirring all the $\text{Mo}_2(\text{O}^\circ\text{Hex})_6$ has reacted and dissolved. The solution was allowed to stand at room temperature for 24 h, during which time red crystals were precipitated. The crystals were collected by filtration and washed with hexane (10 cm³) and toluene (10 cm³) to give $\text{Mo}_2(\text{SeAr}')_4(\text{O}^\circ\text{Hex})_2$ (0.026 g, 0.21 mmol, 33%). IR (KBr disc): 3000m, 2920s, 1595w, 1560w, 1440s, 1400w, 1370m, 1350m, 1335w, 1290m, 1245w, 1230w, 1160w, 1140w, 1080w, 1035vs, 1005vs, 965s, 945m, 880w, 860w, 840vs, 790s, 720w, 700vs, 630sh, 600w, 555w, 540w, 500w, 460w, 450w, 410w, 375w, 345w, 330w, 315w, 295m, 274w, cm⁻¹. ¹H NMR at 25°C (C₆D₆): δ = 6.54 (s, 8H), 2.24 (s, 24H), 2.15 (s, 12H), 1.6 (br, 10H), 0.85 (br, 12H).

$\text{Mo}_2(\text{SeAr}')_4(\text{O}^i\text{Pr})_2$

$\text{Mo}_2(\text{O}^i\text{Pr})_6$ (0.050 g, 0.092 mmol) was dissolved in toluene (20 cm³) at room temperature to generate an orange solution. Mesitylene selenol (0.30 g, 1.5 mmol) was added dropwise with stirring generating a dark-red colour in solution. The mixture was allowed to stand at room temperature for 3 days and then cooled to -20°C for 2 days to produce a mixture of red needles (90%) and yellow plates (10%), both of which were $\text{Mo}_2(\text{O}^i\text{Pr})_2(\text{SeAr}')_4$ (0.035 g, 0.032 mmol, 35%). The crystals were collected by decanting the solution and washing with 10 cm³ of both pentane and diethyl-ether. The filtrate was combined with pentane (10 cm³) and cooled to -20°C to produce a fine orange-red precipitate of $\text{Mo}_2(\text{O}^i\text{Pr})_2(\text{SeAr}')_4$ (0.015 g, combined yield 45%). Found: C, 46.2; H, 4.7; N, 0.0. Calc.: C, 45.7; H, 5.3%. ¹H NMR (C₆D₆): δ = 6.93 (s, 2H), 6.89 (s, 4H), 6.86 (s, 2H), 4.07 (sept, 2H), 2.41 (s, 6H), 2.32 (s, 6H), 2.29 (s, 12H), 1.29 (d, 12H). IR (KBr disc): 2995m, 2942s, 2895s, 2835m, 1580w, 1445s, 1425s, 1360m, 1350m, 1310m, 1275m, 1160w, 1150m, 1115m, 1090s, 1020m, 1004m, 960vs, 835s, 720w, 690w, 600m, 550w, 535w, 460m, 440m, 330w, 290s cm⁻¹.

$\text{M}_2(\text{NMe}_2)_4(\text{SeAr}')_2$ (M = Mo, W)

Mesitylene magnesium bromide (0.46 cm³, 1 M soln in THF) was added to THF (10 cm³) at room temperature. Solid elemental grey selenium (0.36 g, 0.46 mmol) was added and the mixture stirred for 0.5 h until all the selenium had dissolved leaving a clear colourless solution. Solid $\text{Mo}_2\text{Cl}_2(\text{NMe}_2)_4$ (0.100 g, 0.27 mmol) was added and the solution rapidly stirred for 1 min, generating a clear yellow solution. The solution was allowed to stand overnight producing yellow needle-like crystals. The

solution was filtered and the crystals washed with *n*-pentane (10 cm³) and diethyl-ether (10 cm³) to give $\text{Mo}_2(\text{SeAr}')_2(\text{NMe}_2)_4$ (0.060 g, 0.086 mmol, 32%). The filtrate was cooled to -20°C to produce a second crop (0.012 g, 0.0156 mmol overall yield 38%). The crystals were air sensitive and insoluble in hexane, acetone, THF and water. IR (Nujol mull): 1440sh, 1380w, 1233m, 1125m, 1028m, 1010m, 940vs, 937vs, 837m, 710w, 695w, 650w, 550m, 540m, 460w, 440w, 335m. ¹H NMR (C₆D₆): δ = 6.79 (s, 4H), 4.38 (br, 12H), 2.54 (s, 12H), 2.09 (br, 18H). Analogous reaction conditions and reaction scale gave for tungsten; $\text{W}_2(\text{SeAr}')_2(\text{NMe}_2)_4$ (yield 0.061 g, 0.065 mmol). IR (Nujol mull): 1440sh, 1380w, 1335m, 1160w, 1130m, 1110m, 1060m, 1030m, 1010m, 945vs, 840m, 710m, 695m, 550m, 540m, 380w, 340 cm⁻¹. ¹H NMR (C₆D₆): δ = 6.82 (s, 4H), 4.38 (br, 12H), 2.54 (s, 12H), 2.13 (br, 18H). Found: C, 33.2; H, 4.4; N, 4.9. Calc.: C, 33.2; H, 4.9; N, 5.9%.

Reactions involving selenophenol with $\text{M}_2(\text{NMe}_2)_6$ and $\text{M}_2(\text{OR})_6$ compounds (M = Mo, W)

Molybdenum

To $\text{Mo}_2(\text{NMe}_2)_6$ (0.05 g, 0.11 mmol) dissolved in toluene (10 cm³) was added selenophenol (0.25 g, 0.15 mmol), generating a purple colour in solution and a purple precipitate. The reaction was allowed to stand at room temperature for 3 days, and the purple precipitate isolated by filtration, washed with THF (5 cm³), hexane (5 cm³) and toluene (5 cm³). The solid (0.076 g) was insoluble in common solvents, air-stable and seemingly inert to hydrolysis. Found: C, 35.2; H, 2.6; N, 0.7. Calc. for $[\text{Mo}_4(\text{SePh})_{10}\text{Se}_2]\text{H}_2\text{NMe}_2$: C, 34.7; H, 2.9; N, 0.6%. IR (KBr disc): 3020br, 2920m, 2700m br, 2400m br, 1550m, 1530m, 1460m, 1450m, 1425m, 1370m, 1310w, 1285w, 1240w, 1165w, 1140w, 1090w, 1055m, 1005m, 1005s, 990m, 930w, 875m, 835m, 800w, 725s, 680s, 655m, 600sh, 550sh, 510sh, 455m, 410w, 395w, 340w, 310w, 295w cm⁻¹. [Reaction of $\text{Mo}_2(\text{O}^i\text{Bu})_6$ with selenophenol under the same conditions produces a purple solid which has similar IR bands to the above save no stretch at 2700, 2400 and 1450 cm⁻¹, but stretches at 1630 and 3200 cm⁻¹.]

Tungsten

To $\text{W}_2(\text{NMe}_2)_6$ (0.050 g, 0.08 mmol) dissolved in toluene (10 cm³) at room temperature was added selenophenol (0.25 g, 1.59 mmol). This produced an intermediate darkening of the solution to red.

After 1 day at room temperature a black precipitate is produced, which was collected by filtration (after 3 days), washed with hexane (10 cm³), toluene (10 cm³) and diethyl-ether (15 cm³). The precipitate is slightly soluble in THF, air-stable and seemingly inert to hydrolysis. Found: C, 27.7; H, 1.7; N, 0.6. Calc. for $[\text{W}_4(\text{SePh})_{10}\text{Se}_4]\text{H}_2\text{NMe}_2$: C, 28.0; H, 2.1; N, 0.5%. IR (KBr disc): 3020br, 2920m, 2650m br, 2310m br, 1550m, 1530m, 1460m, 1450m, 1425m, 1370m, 1310w, 1285w, 1240w, 1165w, 1140w, 1090w, 1055m, 1005m, 1005s, 990m, 930w, 875m, 835m, 800s, 725s, 680s, 655m, 600sh, 550sh, 510sh, 455m, 410w, 395w, 340w, 310w, 295w cm⁻¹. Reaction involving $\text{W}_2(\text{O}^i\text{Pr})_6 \cdot (\text{HNMe}_2)_2$ with selenophenol under the same conditions gave the same product.

X-Ray Structure Determinations

General operating facilities, procedures and programmes have been previously described.²⁵ A summary of the crystal data is given in Table 1.

$\text{W}_2(\text{SeAr}')_6$

A suitable crystal was located and transferred to the goniostat using standard inert atmosphere handling techniques employed by the IUMSC and cooled to -155°C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located no symmetry or systematic absences, indicating a triclinic space group. Subsequent solution and refinement of the structure confirmed the centrosymmetric choice, $P\bar{1}$.

Data were collected in the usual manner using a continuous θ - 2θ scan with a fixed background. Data were reduced to a unique set of intensities and associated σ in the usual manner. The structure was solved by a combination of direct methods (MULTAN 78) and Fourier techniques. A different Fourier synthesis revealed some but not all, hydrogen atoms. All hydrogen atoms positions were therefore calculated using idealized geometries and $d(\text{C}-\text{H}) = 0.95 \text{ \AA}$. These calculated positions were fixed for the final cycles of refinement.

Data were corrected for absorption. A final difference Fourier was featureless, with the largest peak being $1.19 \text{ e/\AA}^3$ at the metal site.

As shown in the figures and tables, the molecule lies at a crystallographic centre of inversion.

$\text{Mo}_2(\text{SeAr}')_6$

Mounting and cooling were performed identically to the tungsten analogue.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, indicating a triclinic space group. The morphology was essentially the same as the tungsten analogue, and examination of the reciprocal space revealed that the structures are indeed isomorphous.

Data were collected in the usual manner using a continuous θ - 2θ scan with a fixed background. Data were reduced to a unique set of intensities and associated σ in the usual manner. The heavy atom coordinates from the tungsten analogue were used as a starting point for the refinement. All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen parameters. All hydrogen atoms were refined isotropically and non-hydrogen atoms anisotropically in the final cycles.

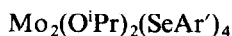
A final difference Fourier was featureless, with the largest peak being $0.45 \text{ e/\AA}^3$. No absorption correction was performed.

$\text{W}_2(\text{O}^i\text{Pr})_2(\text{SeAr}')_4$

A crystal of suitable size was mounted using silicon grease and was transferred to a goniostat where it was cooled to -155°C for characterization and data collection. A search of limited hemisphere of reciprocal space revealed no symmetry or systematic absences. An initial choice of space group $P\bar{1}$ was confirmed by the successful solution of the structure. Following intensity data collection and correction for absorption, data processing gave a residual of 0.010 for 145 unique intensities which had been measured more than once. Four standards measured every 300 data showed no significant trends.

The structure was solved by a combination of direct methods (MULTAN 78) and Fourier techniques. The tungsten and selenium positions were obtained from an E-map. Subsequent iterations of least-squares refinement and different Fourier revealed all of the remaining non-hydrogen atoms. Hydrogen atoms were placed in fixed calculated positions to improve the refinement of the non-hydrogen atoms. Hydrogen thermal parameters were fixed at one plus the isotropic thermal parameter of the atom to which they were bonded.

In the final cycles of refinement all non-hydrogen atoms were refined with anisotropic thermal parameters to a final $R(F) = 0.033$. The final difference map was reasonably clean. There were heavy atom residuals of 0.81 – $1.67 \text{ e/\AA}^3$. All other residual peaks were $0.76 \text{ e/\AA}^3$ or less. The centre of the molecule is at a crystallographic centre of symmetry.



The sample consisted of reddish-orange needles and a minor component (estimated 10%) of yellow plate-like crystals. Both components were examined and transferred to the gonistat where they were cooled to -155°C for characterization and data collection. For the major component a systematic search of limited hemispherical reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to a monoclinic space group. It was later discovered that an *A*-centring was present, the system was not reindexed, leading to the choice of *A2/a* (standard setting *C2/c*).

Data were collected using a continuous θ - 2θ scan with fixed background. Data were reduced to a unique set of intensities and associated σ in the usual manner. The structure was solved by a combination of direct methods (MULTAN 78) and Fourier techniques. A different Fourier synthesis revealed the location of some but not all hydrogen atoms. All hydrogen atoms were assigned idealized geometries $d(\text{C}-\text{H}) = 0.95 \text{ \AA}$. These calculated positions were fixed for the final cycles of refinement. The structure is essentially the same as the tungsten complex above.

The minor component (yellow plates) was also isostructural with the major component (orange-yellow needles). A structure analysis using the same procedure as above was based on a triclinic unit cell with $P\bar{1}$ symmetry.

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