Synthesis and Spectroscopic Characterisation of $[MoO(SR)_4]^-$ (R = C_6H_5, $C_{10}H_7$, 4-$CH_3C_6H_4$, 4-ClC_6H_4, 3-ClC_6H_4, 4-FC_6H_4, 2,6-$Cl_2C_6H_3$, or C_6F_5) Complexes and $[MoO(SC_6F_5)_4]^{2-}$

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The syntheses of $[MoO(SR)_4]^-$ (R = C_6H_5, $C_{10}H_7$, 4-$CH_3C_6H_4$, 4-ClC_6H_4, 3-ClC_6H_4, 4-FC_6H_4, 2,6-$Cl_2C_6H_3$, or C_6F_5) complexes by several different routes are reported. The u.v.–visible, i.r., Raman, e.s.r. spectroscopic and redox properties of these complexes are detailed. The redox potentials of the Mo^{VI}–Mo^V and Mo^V–Mo^{IV} couples correlate with the Hammett function (σ) of the aryl substituent(s); $E^p(Mo^{VI}–Mo^V) = 0.53\sigma + 0.53$ V (*vs.* saturated calomel electrode, s.c.e.) and $E^p(Mo^V–Mo^{IV}) = 0.52\sigma - 0.71$ V (*vs.* s.c.e.). The effect of the electron-withdrawing substituent(s) is also clearly seen in the u.v.–visible spectra, less so in the vibrational spectra, and is absent in the e.s.r. spectra. The synthesis of $[MoO(SC_6F_5)_4]^{2-}$ has been demonstrated and this provides the first spectroscopic comparison of $[MoO(SR)_4]^{n-}$ (*n* = 1 or 2) complexes.

There is considerable current interest in the nature of the molybdenum centres of molybdenum-containing enzymes such as sulphite oxidase, xanthine oxidase, xanthine dehydrogenase, and nitrate reductase.[1] On the basis of the most recent molybdenum *K*-edge extended *X*-ray absorption fine structure (EXAFS),[2] molybdenum(v) e.s.r. spectroscopic data,[3] and the nature of the molybdenum-containing cofactor of the above enzymes,[4] chemistry relevant to these molybdenum centres should involve, as a minimum, molybdenum-(VI), -(V), and/or -(IV) bound to one or more oxo-groups and at least two sulphur-donor ligands.[5] An important class of complexes, in this respect, comprises the mononuclear molybdenum(v) systems $[MoO(SR)_4]^-$;[6–12] the e.s.r. properties of these systems are of intrinsic interest[8] and permit ligand exchange at the MoO^{3+} centre to be monitored for chemical[12] and biochemical[12,13] systems. Wedd and co-workers[9] have shown that these molybdenum(v) complexes are reversibly reduced to their molybdenum(IV) counterparts but that chemical reactions follow the oxidation and result in the appearance of oxidised ligand and a triply bridged binuclear molybdenum(v) complex. Millar and co-workers[14] and Nakamura and co-workers[15] have demonstrated, independently, that sterically hindered thiolate ligands can yield electrochemically stable $[MoO(SR)_4]$ species which have been isolated from chemical oxidation reactions by the former workers, for RS = 2,3,5,6-tetramethylbenzenethiolate or 2,4,6-tri-isopropylbenzenethiolate.

This paper extends the options available for the synthesis of $[MoO(SR)_4]^-$ (R = aryl) complexes and the range of these complexes which has been isolated. Cyclic voltammetric studies of these systems have established a clear correlation between the potential for the Mo^{VI}–Mo^V and Mo^V–Mo^{IV} redox couples and the electron-withdrawing nature of the substituent(s) on the aryl ring. These results encouraged the synthesis and isolation of $[MoO(SC_6F_6)_4]^{2-}$.

Experimental

All syntheses and preparation of solution samples for spectroscopy were carried out under an atmosphere of dinitrogen using standard vacuum and Schlenk-line techniques. Solvents were freshly distilled prior to use from an appropriate drying agent under an atmosphere of dinitrogen and deoxygenated immediately prior to use by repeated evacuation and purging with dinitrogen. Chemicals were used as obtained from Aldrich Chem. Co. or Lancaster Synthesis.

U.v.–visible spectra were recorded on a Shimadzu 260 spectrometer for solutions in 0.1-cm matched silica cells, i.r. spectra on a Perkin-Elmer 577 spectrometer with the compound mulled in Nujol and held between CsI plates, Raman spectra on a Spex 1403 085m double beam spectrometer with a KBr disc sample, and e.s.r. spectra on a Varian E-112 spectrometer at *X*-band frequency (frozen solution spectra were recorded at 77 K using liquid dinitrogen as coolant, with an Oxford Instruments ESR9 cryostat). Electrochemical data were obtained using a PAR model 175 waveform generator and model 173 potentiostat. The cyclic voltammograms were recorded for solutions (*ca.* 2 mmol dm^{-3}) in MeCN at a vitreous carbon electrode with $[NBu_4][BF_4]$ (*ca.* 0.2 mol dm^{-3}) as the supporting electrolyte. Microanalyses were accomplished by the staff of the Microanalytical Laboratory of The Chemistry Department, Manchester University.

Syntheses.—The compounds described herein were synthesised by one of four routes, an example of each route is detailed below.

Route A. Tetraethylammonium tetrakis(benzenethiolato)-oxomolybdate(v) $[NEt_4][MoO(SC_6H_5)_4]$. This compound was prepared as described previously from $[MoOCl_3(thf)_2]$ (thf = tetrahydrofuran), benzenethiol, triethylamine, and tetraethylammonium iodide (1:4:4:1.2) in MeCN.[6]

Route B. Tetraethylammonium tetrakis(2-naphthalenethiolato)oxomolybdate(v) $[NEt_4][MoO(SC_{10}H_7)_4]$. The compound $[MoCl_3(thf)_3]$[16] (0.71 g, 1.7 mmol) was dissolved in thf (10 cm^3). Triethylamine (0.8 g, 8.49 mmol), 2-thionaphthol (1.36 g, 8.49 mmol), 4-methylpyridine *N*-oxide (0.185 g, 1.70 mmol), and thf (10 cm^3) were combined in a pressure-equilibrated dropping funnel and added dropwise to the stirred solution of $[MoCl_3(thf)_3]$. A blue solution resulted, the volume of this was reduced to *ca.* 3 cm^3 by evaporation under reduced pressure and a MeOH solution (20 cm^3) of $[NEt_4]I$ (0.55 g, 2.12 mmol) was added. The resultant blue precipitate was recovered by filtration, washed with MeOH (5 × 10 cm^3), and dried *in vacuo.*

Route C. Tetraethylammonium oxotetrakis(2,3,4,5,6-pentafluorobenzenethiolato)molybdate(v) $[NEt_4][MoO(SC_6F_5)_4]$. This compound was prepared by thiol exchange.[17] The compound $[NEt_4][MoO(SPh)_4]$ (0.74 g, 1.09 mmol) was dissolved

Table 1. Synthetic and analytical data for compounds containing $[MoO(SR)_4]^{n-}$ (n = 1 or 2) anions

			Analysis */%						
Compound	Synthetic route	Yield/%	C	H	Cl	F	Mo	N	S
(**1**) $[NEt_4][MoO(SC_6H_5)_4]$	A	77	56.4	6.0			14.2	2.1	18.9
	B	35	56.1	6.2			14.1	2.2	18.7
			(56.6)	(5.9)			(14.0)	(2.1)	(18.9)
(**2**) $[NEt_4][MoO(SC_{10}H_7)_4]$	B	33	64.6	5.5			8.9	1.3	15.4
			(65.6)	(5.5)			(10.9)	(1.5)	(14.5)
(**3**) $[NEt_4][MoO(S\text{-}4\text{-}CH_3C_6H_4)_4]$	A	55	59.3	6.7			12.8	1.7	16.9
			(58.8)	(6.6)			(13.2)	(1.9)	(17.5)
(**4**) $[NEt_4][MoO(S\text{-}4\text{-}ClC_6H_4)_4]$	A	51	48.2	4.5	17.6		11.9	1.9	16.1
			(47.7)	(4.5)	(17.6)		(11.9)	(1.7)	(15.9)
(**5**) $[NEt_4][MoO(S\text{-}3\text{-}ClC_6H_4)_4]$	A	73	46.7	4.4	17.7		11.3	1.7	15.5
			(47.7)	(4.5)	(17.6)		(11.9)	(1.7)	(15.9)
(**6**) $[NEt_4][MoO(S\text{-}4\text{-}FC_6H_4)_4]$	A	29	51.2	4.9		10.0	12.7	2.2	16.7
			(51.2)	(4.8)		(10.1)	(12.8)	(1.9)	(17.1)
(**7**) $[NEt_4][MoO(S\text{-}2,6\text{-}Cl_2C_6H_3)_4]$	A	36	40.2	3.5	28.6		9.8	2.0	12.8
			(40.2)	(3.3)	(29.7)		(10.1)	(1.5)	(13.4)
(**8**) $[NEt_4][MoO(SC_6F_5)_4]$	C	73	37.9	2.1		34.8	8.9	1.3	12.4
			(37.0)	(1.9)		(36.6)	(9.2)	(1.3)	(12.3)
(**9**) $[NHEt_3]_2[MoO(SC_6F_5)_4]$	D	80	38.5	2.8		34.7	8.2	2.2	11.5
			(38.5)	(2.9)		(34.7)	(8.5)	(2.5)	(11.4)

* Calculated values are given in parentheses.

in CH_2Cl_2 (40 cm^3), pentafluorobenzenethiol (1.74 g, 8.74 mmol) was added and the solution stirred. After *ca.* 1 h a purple precipitate formed, which was recovered by filtration and redissolved in CH_2Cl_2 (40 cm^3). Pentafluorobenzenethiol (0.87 g, 4.36 mmol) was added and the solution stirred until a precipitate formed. This was recovered by filtration and the process repeated once again. The final precipitate was recovered by filtration, washed with MeOH (3 × 5 cm^3), and dried *in vacuo*.

Route D. Triethylammonium oxotetrakis(2,3,4,5,6-*pentafluorobenzenethiolato*)*molybdate*(IV) $[NHEt_3]_2[MoO(SC_6F_5)_4]$. The compound $[MoOCl_2(PPh_2Me)_3]$[18] (0.56 g, 0.7 mmol) was dissolved in CH_2Cl_2 (15 cm^3). Dichloromethane (5 cm^3), pentafluorobenzenethiol (0.58 g, 2.9 mmol), and triethylamine (0.29 g, 2.9 mmol) were combined in a pressure-equilibrated dropping funnel and added dropwise to the stirred solution of $[MoOCl_2(PPh_2Me)_3]$. After *ca.* 2 h a grey precipitate resulted which was recovered by filtration, washed with CH_2Cl_2 (3 × 5 cm^3), dried *in vacuo*, and stored under a dinitrogen atmosphere.

All other compounds reported herein were synthesised by a variation on one of the above methods, in which the appropriate thiol was substituted (4 equivalents with respect to the molybdenum starting material) for the named thiol in the synthetic method (Table 1).

Results and Discussion

Synthesis.—The primary synthetic route to complexes $[MoO(SR)_4]^-$ (R = aryl) described here was that of Boyd *et al.*[6] (route A). Routes B and C, however, offer alternative methods and have enabled us to synthesise the thionaphthol and pentafluorobenzenethiol complexes which were unobtainable by route A. Route B involves a 'self assembly' reaction in which both halide displacement and oxo transfer from an amine oxide to form the $\{MoO\}^{3+}$ core occur. As compared with route A, route B gives lower yields and uses a starting material that is more difficult to prepare, however, it can provide a useful alternative when route A fails.

The synthesis of the pentafluorobenzenethiolate complex (**8**) could not be effected by either route A or B and this suggests that the highly electron-withdrawing nature of the aryl substituents reduces the nucleophilicity of the thiolate sulphur. However, thiol exchange which has previously been used with bidentate thiols[12,17] provided a convenient and facile route to this complex. The fact that $[MoO(SC_6F_5)_4]^-$ (**8**) was the most easily reduced anion (see later) suggested that direct synthesis of $[MoO(SC_6F_5)_4]^{2-}$ (**9**) might be possible. Subsequent synthesis of (**9**) was effected by route D, involving ligand substitution by monodentate thiolate at a molybdenum(IV) centre. However, route D has not yet been demonstrated to have a general applicability.

Table 2. U.v.–visible absorption spectra data for $B^+{}_n[MoO(SR)_4]^{n-}$ at *ca.* 293 K

Compd.	λ/nm (10^{-3} × ε/dm^3 mol^{-1} cm^{-1})	Solvent
(**1**)*	602 (6.4) 328 (sh) 288 (sh)	MeCN
(**2**)	614 (4.7) 328 (sh) 314 (sh) 292 (sh)	MeCN
(**3**)*	612 (6.8) 360 (sh) 330 (sh) 284 (sh)	CH_2Cl_2
(**4**)	601 (5.5) 332 (sh) 288 (sh)	CH_2Cl_2
(**5**)	598 (5.2) 324 (sh) 290 (sh)	MeCN
(**6**)	600 (3.6) 360 (sh) 325 (12.8) 280 (sh)	MeCN
(**7**)	579 (2.4) 316 (sh) 265 (2.5)	MeCN
(**8**)	556 (2.1) 324 (sh) 279 (4 330)	CH_2Cl_2
(**9**)	450 (2.2) 340 (sh) 299 (sh)	MeCN

* *cf.* Ref. 8.

U.v.–Visible Spectroscopy.—The u.v.–visible spectroscopic data obtained for these complexes in solution are summarised in Table 2. The main feature of interest in the spectra of the molybdenum(V) complexes is the low-energy band centred around 600 nm with $\varepsilon < 2\,000$ dm^3 mol^{-1} cm^{-1}. The band maximum shifts to higher energy as the substituent(s) on the aryl group become more electron withdrawing which is consistent with the band having some ligand-to-metal charge transfer (l.m.c.t.) characteristic, an assignment proposed for the 'MoS_4' chromophore by Hanson *et al.*[8] That this band is found at lower energy than the lowest-energy band with a high (>500 dm^3 mol^{-1} cm^{-1}) absorption coefficient for $[MoOX_{4/5}]^{1-/2-}$ (X = Br or NCS) which has been assigned as a l.m.c.t. process[19] is also qualitatively consistent with the

Table 3. Vibrational spectroscopic data for $B^+{}_n[MoO(SR)_4]^{n-}$ (n = 1 or 2): position of the $Mo{=}O_t$ stretch; B = $[NEt_4]$

	$\nu(Mo{=}O_t)/cm^{-1}$	
Compound	I.r.[a]	Raman[b]
(1)[c]	929	928
(2)	*d*	929
(3)	934	930
(4)	938[e]	925
(5)	930	930
(6)	932	925
(7)	955	960
(8)	982	*f*
(9)[g]	927	927

[a] Sample mulled in Nujol. [b] Sample compressed in KBr disc with 458-nm excitation. [c] *cf.* Ref. 8. [d] Unassignable. [e] Broad peak. [f] Sample burnt up in laser. [g] B = $[NHEt_3]$.

Table 4. E.s.r. properties of $[NEt_4][MoO(SR)_4]$ at *X*-band frequency in MeCN solution; $\bar{A}$ in units of 10^{-4} cm^{-1}

Compound	Room-temperature solution, 293 K	Frozen solution, 77 K
(1)*	$\bar{g}$ = 1.989 $\bar{A}$ = 32.5	$g_{\parallel}$ = 2.015 $g_{\perp}$ = 1.980
(2)	$\bar{g}$ = 1.989 $\bar{A}$ = 32.5	g_1 = 2.015 g_2 = 1.987 g_3 = 1.975
(3)*	$\bar{g}$ = 1.990 $\bar{A}$ = 32.5	g_1 = 2.014 g_2 = 1.983 g_3 = 1.987
(4)	$\bar{g}$ = 1.989 $\bar{A}$ = 32.5	$g_{\parallel}$ = 2.014 $g_{\perp}$ = 1.974
(5)	$\bar{g}$ = 1.989 $\bar{A}$ = 32.5	g_1 = 2.014 g_2 = 1.982 g_3 = 1.973
(6)	$\bar{g}$ = 1.991 $\bar{A}$ = 32.5	g = 1.998 (broad)
(7)	$\bar{g}$ = 1.988 $\bar{A}$ = 34.0	$g_{\parallel}$ = 2.015 $g_{\perp}$ = 1.986
(8)	$\bar{g}$ = 1.990 $\bar{A}$ = 34.8	$g_{\parallel}$ = 2.020 $g_{\perp}$ = 1.986

* *cf.* Ref. 8.

arguments of optical electronegativity advanced by Jørgensen.[20] It is likely that the expected low-energy *d–d* transition involving the $\{MoO\}^{3+}$ fragment is masked by this dominant c.t. process.

Vibrational Spectroscopy.—The main feature of interest in both the i.r. and Raman spectra of these complexes is the position of the $Mo{=}O_t$ stretch; the data are summarised in Table 3. For complexes of the type $[MoO(SR)_4]^-$ with very electron-withdrawing aryl substituents, $\nu(Mo{=}O_t)$ shifts to higher wavenumber but the effect is small and for five of the compounds there is no significant change. A shift in $\nu(Mo{=}O_t)$ to higher wavenumber as the electron-withdrawing nature of the substituents increases would be expected, in principle, because the O–Mo π bonding should be enhanced as the electron-withdrawing nature of the aryl substituents increases. This appears to be true only for the C_6F_5 complex.

The Mo–O_t stretch for $[MoO(SR)_4]^-$ is found at lower wavenumber than that observed in other five-co-ordinate oxomolybdenum(V) complexes,[21] *e.g.* $[MoOX_4]^-$ (X = Cl, Br, or I) where $\nu(Mo{=}O_t)$ 1 000—1 020 cm^{-1}. This difference is consistent with the greater π-donor ability of thiolato *versus* halide ligands, reducing the amount of O p_π to Mo d_π ligand-to-metal bonding.

Table 5. Cyclic voltammetry data for $[NEt_4][MoO(SR)_4]$

		Mo^V–Mo^{IV} [a]			Mo^{VI}–Mo^V [a]		
Compd.	$E^p_{\frac{1}{2}}$	E^p_{ox}	E^p_{red}	I^p_{ox}/I^p_{red}	E^p_{ox} [b]	E^p_{ox} Δ[c] – $E^p_{\frac{1}{2}}$	Hammett function[d]
(1)	−0.75	−0.71	−0.79	0.97[e]	0.49	1.24	0
(2)	−0.66	−0.63	−0.69	1.00[e]	0.50	1.16	
(3)	−0.78	−0.74	−0.82	0.91[e]	0.43	1.21	−0.17
(4)	−0.59	−0.55	−0.62	1.00[e]	0.60	1.19	0.23
(5)	−0.55	−0.52	−0.58	0.84	0.64	1.19	0.37
(6)	−0.65	−0.60	−0.68	0.88	0.59	1.23	0.06
(7)	−0.52	−0.48	−0.55	0.42	0.81	1.33	0.40
(8)	−0.005	0.04	−0.05	0.94	1.20	1.21	1.22

[a] Volts *versus* s.c.e. with $[NBu_4][BF_4]$ supporting electrolyte in MeCN at *ca.* 293 K. [b] Irreversible oxidation. [c] Average Δ = 1.22. [d] See refs. 21 and 22. [e] See refs. 19 and 20.

E.S.R. Spectroscopy.—The e.s.r. data obtained for the complexes synthesised in this study are summarised in Table 4; the data are consistent with those of Hanson *et al.*[8] who have extensively studied the e.s.r. properties of $[MoO(SC_6H_5)_4]^-$.

The value of *g* obtained at *X*-band for fluid solutions shows little variation with the nature of the aryl group suggesting that the unpaired electron does not interact to any great extent with the atoms beyond the sulphur of the ligand. In each case the fluid solution spectrum at *X*-band, which displayed very narrow (*ca.* 2 G, 2 × 10^{-4} T) linewidths, was used as a probe of the number of paramagnetic species in solution and each of the spectra was consistent with there being only one such species.

The frozen-solution spectra at *X*-band exhibit either axial or rhombic type signals. In some cases features due to $^{95,97}Mo$ hyperfine coupling were observed at both high and low field of the central resonances. However, since these were not necessarily principal *A* values no numerical data for these are reported.

Electrochemistry.—Cyclic voltammograms of these compounds were recorded in MeCN and the data obtained are presented in Table 5. The data for $[MoO(SR)_4]^-$ show a general trend that, as the aryl substituents become more electron withdrawing, the potential for reduction and oxidation moves in the expected sense.

The ease of reduction (*i.e.* the value of E^p_{red}) of $[NEt_4][MoO(SR)_4]$ may be correlated with the Hammett functions of the substituent groups on the arenethiolate.[22] Hammett functions are derived by considering the pK_a of the substituent on benzoic acid *versus* the pK_a of unsubstituted benzoic acid. For polysubstituted aryl groups it has been suggested that Hammett functions (σ) are additive.[23,24] Basically, a Hammett function may be considered as a measure of the electron-withdrawing power of the substituents, a negative value indicating electron donation (Table 5).

A plot of E^p_{red} for the Mo^V–Mo^{IV} couple *versus* σ (Figure 1) correlates the potential of this reduction process with the electron-withdrawing properties of the aryl substituents. The graph is essentially a straight line of the form $E^p_{red} = 0.52\sigma - 0.71$ V. The Mo^{VI}–Mo^V oxidation potential also correlates linearly with the Hammett function (Figure 1), giving a line of the form $E^p_{ox} = 0.53\sigma + 0.53$ V. The gradient is virtually the same for both these plots which reinforces the concept of the electron-withdrawing nature of the substituent group on the thiol being the dominant effect in determining the redox potential of the $[MoO(SR)_4]^-$ complexes.

A plot of Hammett values *versus* redox potentials has been undertaken for iron–sulphur clusters of the type [Fe$_4$S$_4$-

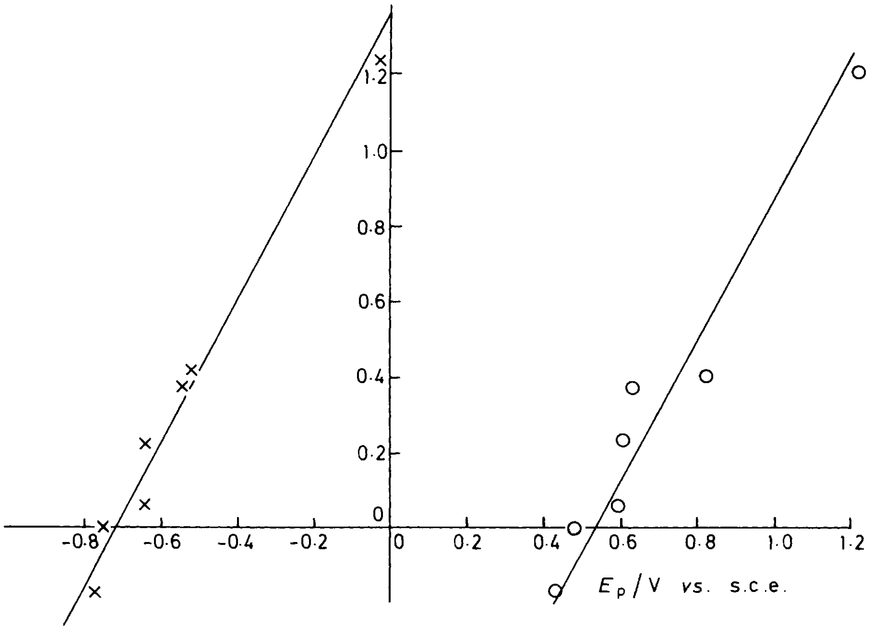

Figure 1. Graph of Hammett function *versus* electrode potential for $[MoO(SR)_4]^-$: (×) Mo^V–Mo^{IV}; (○) Mo^{VI}–Mo^V

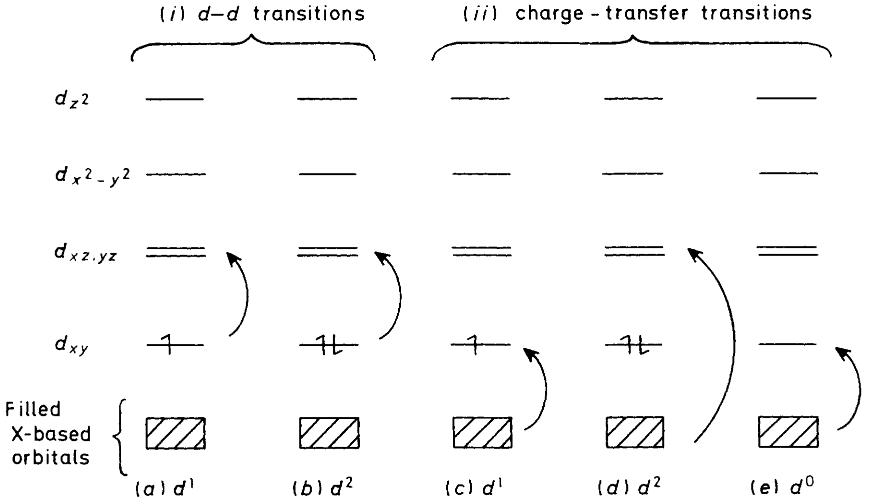

Figure 2. Idealized orbital stacking diagram for $[MEX_4]^{n-}$, in C_{4v} point symmetry, where E is a significant π-donor ligand. Arrows indicate expected lowest-energy process

$(S\text{-}4\text{-}XC_6H_4)_4]^{2-/3-}$ ($X = CH_3$, H, or NMe_3^+) and a linear relationship of the type $E_{\frac{1}{2}} = 0.295\sigma - 1.04$ V was obtained (for potentials *versus* s.c.e.).[22] This was interpreted also to mean that the nature of the thiolate substituents determined the redox potentials. From a comparison of the gradients obtained for the $[Fe_4S_4(SR)_4]^{2-/3-}$ cluster and $[MoO(SR)_4]^{1-/2-}$ it would appear that the effect of the election-withdrawing nature of the aryl substituent on the reduction potential is greater in the case of the $\{MoO\}^{3+}$ core than for the $\{Fe_4S_4\}^{2+}$ core. However, over-interpretation of these expressions should be avoided.[25]

$[MoO(SR)_4]^{n-}$ (*n* = 1 *or* 2): *a comparison of* Mo^V *and* Mo^{IV}.—Within the vibrational spectra, $\nu(Mo{=}O_t)$ occurs at higher wavenumber for $[MoO(SC_6F_5)_4]^-$ (**8**) than for $[MoO(SC_6F_5)_4]^{2-}$ (**9**) and this is consistent with the decreased electron density of Mo^V *versus* Mo^{IV} encouraging an increased O p_π to Mo d_π donation, leading to a stronger $Mo{=}O_t$ bond.

The cyclic voltammograms of $[MoO(SC_6F_5)_4]^{n-}$ (*n* = 1 or 2) (**8**) and (**9**) were found to be identical confirming the redox relationship of these two compounds. The u.v.–visible spectrum of $[MoO(SC_6F_5)_4]^{2-}$ (**9**) exhibits a virtually featureless visible region, which is in contrast to that of $[MoO(SC_6F_5)_4]^-$ (**8**) which has a prominent band at 556 nm (ε = 2 100 $dm^3\ mol^{-1}\ cm^{-1}$). This lack of absorbance in the visible region for MoO^{2+} is paralleled by the oxomolybdenum enzyme sulphite oxidase, which also exhibits a loss of features in the visible region on reduction.[26] These similarities support the proposition that there is thiolate-type sulphur bound to molybdenum in the oxomolybdoenzymes. A qualitative explanation of these observations is outlined in Figure 2 and supported by consideration of the structurally related $[Re^{V}OX_4]^-$ (d^2) and $[Re^{VI}OX_5]^-$ (d^1) species. This 'bleaching' of the visible region is also observed for the rhenium complexes where X = Cl, when hydrochloric acid solutions of the metal complex are reduced.[27] The orbital stacking diagram for idealized C_{4v} symmetry (see Figure 2) demonstrates that for the expected $(d_{xy})^1$ or $(d_{xy})^2$ ground state, where l.m.c.t. processes are important, these are likely to occur at higher energy for d^2 *vs.* d^1 systems as observed for the $[ReOCl_{4/5}]^-$ pair. Similarly when the effects of interelectron repulsions are considered for the *d–d* transitions these shift the lowest-energy band down in energy *versus* the equivalent d^1 complex, *viz.* $[ReOCl_4]^-$ has the lowest-energy band at 8 440 cm^{-1} [28] whereas that for $[ReOCl_5]^-$ occurs at 11 200 cm^{-1}.[29]

Thus, the assignment of the lowest-energy band of compound (**8**) at 17 990 cm^{-1} to a sulphur-to-metal charge-transfer process (this may mask the weaker *d–d* transition expected in this region), which shifts to higher energy at 22 220 cm^{-1} on reduction without a gross structural change, and results in the appearance of weak features at 7 090 and 8 580 cm^{-1}, is consistent with the description shown in Figure 2. This interpretation is also consistent with the recent study[30] on $[ReE(SCH_2CH_2S)_2]^-$, where *E* = O or S. Also, these arguments are analogous to those presented[14] for the complexes $[MoO(S\text{-}2,4,6\text{-}Pr^i_3C_6H_2)_4]^{n-}$ (*n* = 0 or 1) where the intense absorption at 12 450 cm^{-1} is considerably red shifted (by *ca.* 5 000 cm^{-1}) on going from *n* = 1 to *n* = 0, as illustrated in Figure 2.

Electrochemical studies on oxomolybdenum(V) tetrakis(arenethiolate) complexes have shown that they are the central members of the electron-transfer series $[MoO(SR)_4] \underset{E_{ox}}{\overset{(1)}{\rightleftharpoons}} [MoO(SR)_4]^- \underset{E_{red}}{\overset{(2)}{\rightleftharpoons}} [MoO(SR)_4]^{2-}$ as reported by Millar and co-workers.[14] However, these workers demonstrated the chemical oxidation [reaction (1)] required sterically bulky aromatic substituent groups to stabilise the molybdenum(VI) complex (and thereby decrease E_{ox} relative to R = Ph); it is now shown that the synthesis of the reduced species [equivalent to reaction (2)] is facilitated by the presence of electron-withdrawing substituents on the aromatic thiolate (and a consequent increase of E_{red} relative to R = Ph).

Conclusions

The synthesis of complexes of the type $[MoO(SR)_4]^-$ has been effected by three synthetic routes. The physical properties of the complexes, especially the Mo^{VI}–Mo^{V} and Mo^{V}–Mo^{IV} redox properties and the lowest visible transitions, may, in general, be related to the electron-withdrawing-donating properties of the aryl group substituents. More specifically, the synthesis of $[MoO(SC_6F_5)_4]^{2-}$ has allowed a spectroscopic comparison between such molybdenum-(V) and -(IV) analogues.

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