Notes

Synthesis and Properties of Dioxo-osmium(VI) Compounds of Thio- and Seleno-ethers†

Stephen K. Harbron and William Levason *
Department of Chemistry, The University, Southampton SO9 5NH

A series of *trans*-dioxo-osmium(VI) complexes $[OsO_2X_2L_2]$ and $[OsO_2X_2(L\text{-}L)]$ [X = Cl or Br; L = SMe_2; L–L = $MeSCH_2CH_2SMe$, $o\text{-}C_6H_4(SMe)_2$, $MeSeCH_2CH_2SeMe$, or $o\text{-}C_6H_4(PPh_2)(SMe)$] have been prepared from OsO_4 and the ligands in ethanol–HX solution. The complexes have been characterised by i.r., electronic, and ^1H n.m.r. spectroscopy.

We have recently shown[2] that osmium tetraoxide and dithioether ligands (*e.g.* $MeSCH_2CH_2SMe$) react under reflux (2—3 h) in a mixture of concentrated hydrochloric acid and ethanol to form the dark green osmium(IV) complexes, $[OsCl_4(\text{dithioether})]$. Subsequently we found that better yields of the Os^{IV} complexes were obtained from $Na_2[OsCl_6]$ and the ligand in 2-methoxyethanol,[2] whilst under prolonged reflux with excess ligand, Os^{III} derivatives $[OsCl_3(\text{dithioether})_{1.5}]$ result.[3] We have reinvestigated the OsO_4–HX (X = Cl or Br)–dithioether–ethanol reactions, and find that under mild conditions, *trans*-dioxo-osmium(VI) complexes can be isolated. A variety of related *trans*-$[OsO_2]^{2+}$ (osmyl) complexes are known,[4] but no examples with thio- or seleno-ethers have been reported; indeed complexes of Group 6B donor ligands with any high oxidation state metal ions are rare.[2,5]

Results and Discussion

The addition of two mol equivalents of SMe_2 to a solution of OsO_4 in a mixture of concentrated HX (X = Cl or Br) and ethanol at room temperature gave moderate yields (*ca.* 35%) of the orange-brown complexes $[OsO_2X_2(SMe_2)_2]$. The corresponding reactions using one equivalent of L–L [$MeSCH_2CH_2SMe$, $o\text{-}C_6H_4(SMe)_2$, or $o\text{-}C_6H_4(PPh_2)(SMe)$] gave $[OsO_2X_2(L\text{-}L)]$. (Table 1). The dark green filtrates obtained after separation of the osmyl complexes contain the known[2] Os^{IV} dithioether complexes. Curiously the ligand *cis*-MeSCH=CHSMe rapidly reduced the OsO_4–HCl–EtOH mixture to green $[OsCl_4(MeSCHCHSMe)]$, and the osmyl complex was not isolated. In contrast arylthioethers, SPh_2 or $PhSCH_2CH_2SPh$, did not react with the OsO_4–HX–EtOH mixture, even after several days at room temperature. The selenoethers, $SeMe_2$ and $MeSeCH_2CH_2SeMe$ gave poor yields of the Os^{VI} complexes, but $PhSeCH_2CH_2SePh$ and $TeMe_2$ were rapidly oxidised by OsO_4–HX–EtOH, and no evidence for an Os^{VI} complex was obtained.

Spectroscopic data on the isolated complexes are listed in Table 1, along with data on $[OsO_2X_4]^{2-}$ (X = Cl or Br) for comparison. All the complexes show a single very strong absorption in the i.r. spectra at 840—850 cm^{-1}, characteristic of

Table 1. Spectroscopic data for the complexes *trans*-$[OsO_2X_2L_2]$ and *trans*-$[OsO_2X_2(L\text{-}L)]$

		I.r.[a]/cm^{-1}		^1H N.m.r.[b]		
Complex	Colour	$\nu(OsO_2)$	$\nu(OsX)$	Solvent	$\delta(Me)$/p.p.m.	$10^{-3}E_{max}/cm^{-1}$ ($\varepsilon/dm^3\ cm^{-1}\ mol^{-1}$)
$[OsO_2Cl_2(SMe_2)_2]$	Orange-brown	850	310	$CDCl_3$	2.85 (0.73)	26.90 (615), 19.4 (210)[c]
$[OsO_2Br_2(SMe_2)_2]$	Orange-brown	850	215	$CDCl_3$	3.00 (0.88)	26.60 (740), 19.5 (sh)[c]
$[OsO_2Cl_2(MeSCH_2CH_2SMe)]$	Light brown	850	305	$(CD_3)_2SO$	2.75, 2.85 (0.73)	27.77 (360), 24.35 (sh), 20.8 (sh)[d]
$[OsO_2Br_2(MeSCH_2CH_2SMe)]$	Dark brown	850	195	$(CD_3)_2SO$	2.80, 2.95 (0.80)	26.45 (1 570), 22.22 (1 095), 18.8 (sh)[d]
$[OsO_2Cl_2\{o\text{-}C_6H_4(SMe)_2\}]$	Dark brown	850	312	*e*		
$[OsO_2Br_2\{o\text{-}C_6H_4(SMe)_2\}]$	Dark brown	850	205	*e*		
$[OsO_2Cl_2\{o\text{-}C_6H_4(PPh_2)(SMe)\}]$	Orange-brown	842	320	$(CD_3)_2SO$	3.24 (0.84)	30.50 (2 400), 19.5 (sh)[d]
$[OsO_2Br_2\{o\text{-}C_6H_4(PPh_2)(SMe)\}]$	Orange-brown	842		$(CD_3)_2SO$	3.32 (0.92)	28.40 (2 830), 22.3 (sh) (420),[d] 20.5 (sh)
$[OsO_2Cl_2(SeMe_2)_2]$	Orange	845	310	$CDCl_3$	2.65 (0.65)	26.45 (475), 20.6 (94), *ca.* 20.0 (sh)[c]
$[OsO_2Br_2(SeMe_2)_2]$	Light brown	845		$CDCl_3$	2.80 (0.80)	32.5 (21 300), 25.77 (1 020), 21.45 (sh) (140)[c]
$[OsO_2Cl_2(MeSeCH_2CH_2SeMe)]$	Light brown	845	300	$(CD_3)_2SO$	2.50, 2.70 (0.58)	25.88 (850), 19.6 (96)[d]
$[OsO_2Br_2(MeSeCH_2CH_2SeMe)]$	Light brown	845	200br	*e*		27.7 (sh), 24.05 (–), 22.32 (–), *ca.* 18.8 (sh)[d,f]
$Cs_2[OsO_2Cl_4]$	Buff	845	308			28.35 (600), 24.40 (sh)[g]
$Cs_2[OsO_2Br_4]$	Orange-brown	842				33.00 (9 000), 22.70 (sh) (180)[h]

[a] As Nujol mulls, range 4 000—180 cm^{-1}. [b] Co-ordination shifts are given in parentheses. Free ligand $\delta(Me)$: SMe_2, 2.12; $SeMe_2$, 2.0; $MeSCH_2CH_2SMe$, 2.07; $o\text{-}C_6H_4(PPh_2)(SMe)$, 2.4; $MeSeCH_2CH_2SeMe$, 2.02. [c] In $CHCl_3$. [d] In $(CH_3)_2SO$. [e] Decomposition. [f] Solution decomposes rapidly ε not recorded. [g] In 1 mol dm^{-3} HCl. [h] In 1 mol dm^{-3} HBr.

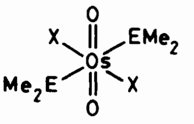
---

† Taken as 'Co-ordination Chemistry of Higher Oxidation States.' Part 14.[1]

Table 2. Elemental analyses for the complexes *trans*-$[OsO_2X_2L_2]$ and *trans*-$[OsO_2X_2(L\text{-}L)]$

Compound	Analysis • (%) C	H	Os	Yield (%)
$[OsO_2Cl_2(SMe_2)_2]$	11.8 (11.5)	3.0 (2.9)	45.8 (45.6)	34
$[OsO_2Br_2(SMe_2)_2]$	9.4 (9.5)	2.4 (2.4)	39.8 (37.5)	35
$[OsO_2Cl_2(MeSCH_2CH_2SMe)]$	11.6 (11.6)	2.4 (2.4)	44.2 (45.8)	56
$[OsO_2Br_2(MeSCH_2CH_2SMe)]$	9.6 (9.5)	2.1 (2.0)	37.9 (37.7)	55
$[OsO_2Cl_2\{o\text{-}C_6H_4(SMe)_2\}]$	20.6 (20.7)	2.1 (2.2)	39.9 (41.0)	22
$[OsO_2Br_2\{o\text{-}C_6H_4(SMe)_2\}]$	17.5 (17.4)	1.8 (1.8)	33.3 (34.4)	21
$[OsO_2Cl_2\{o\text{-}C_6H_4(PPh_2)(SMe)\}]$	38.0 (37.6)	2.7 (2.8)	31.2 (31.4)	36
$[OsO_2Br_2\{o\text{-}C_6H_4(PPh_2)(SMe)\}]$	31.5 (31.9)	2.3 (2.4)	25.7 (26.6)	36
$[OsO_2Cl_2(SeMe_2)_2]$	9.3 (9.4)	2.3 (2.3)	38.6 (37.7)	17
$[OsO_2Br_2(SeMe_2)_2]$	8.1 (8.0)	2.0 (2.0)	31.9 (31.7)	17
$[OsO_2Cl_2(MeSeCH_2CH_2SeMe)]$	9.6 (9.4)	2.1 (2.0)	37.3 (37.3)	25
$[OsO_2Br_2(MeSeCH_2CH_2SeMe)]$	7.8 (8.0)	1.6 (1.7)		5

• Calculated values in parentheses.



(I)

a *trans*-$[OsO_2]^{2+}$ group.[4,6,7] Medium intensity bands at *ca.* 300 cm^{-1} (Cl) and *ca.* 200 cm^{-1} (Br) are tentatively assigned to osmium–halogen stretches, although $\nu[Os\text{–}S(Se)]$ and deformations of the osmyl group are expected in this region. The electronic spectra of the complexes are similar in profile to those of $[OsO_2X_4]^{2-}$, and the recently reported $[OsO_2X_2(PR_3)_2]$,[6,7] and the main bands are clearly due to $L \rightarrow Os$ charge-transfer transitions. Very weak absorptions are just evident in the low-energy tails of the charge-transfer bands, and these are probably the *d–d* transitions expected [8] for the Os^{VI} ion. Like all the known [4] osmyl complexes, the present examples are diamagnetic, with the ground-state configuration of $(d_{xy})^2$.

The ^1H n.m.r. spectra of $[OsO_2X_2(EMe_2)_2]$ (E = S or Se) in $CDCl_3$ show single $\delta(Me)$ resonances, indicating only one isomer is present, probably the all-*trans* form (I). The complexes of the bidentate ligands L–L are not sufficiently soluble in $CDCl_3$, but spectra were obtained in $(CD_3)_2SO$, except for those of the $o\text{-}C_6H_4(SMe)_2$ compounds which decomposed immediately. The spectra of $[OsO_2X_2(MeECH_2CH_2EMe)]$ show the two $\delta(Me)$ resonances expected due to the presence of *meso-* and DL-forms of the co-ordinated ligand. The slightly smaller co-ordination shifts observed in the latter complexes are expected since here the MeE groups are *trans* to halide, which have lower *trans* influence than the EMe_2 in (I).

The reaction of RuO_4 in aqueous HCl and a variety of thioethers (including SMe_2, SPh_2, and $PhSCH_2CH_2SPh$) even at 0 °C, instantly produced a black precipitate, $RuO_2{\cdot}nH_2O$, and mixtures of the corresponding sulphoxides and sulphones. The same results were obtained using preformed $[RuO_2Cl_4]^{2-}$ as starting material.

The complexes described above are unusual as they contain ligands which are only moderate σ-donors bound to a metal in a high formal oxidation state (M^{VI}). The only other examples of M^{VI} thioethers reported appear to be of W^{VI} *viz.* $2WSCl_4{\cdot}MeSCH_2CH_2SMe$,[9] $[WCl_6(SMe_2)]$, and $[WCl_6(MeSCH_2CH_2SMe)]$,[10] and we know of no selenoethers bound to a metal in oxidation state greater than +4.[5]

Experimental

Physical measurements were made as described elsewhere. Osmium was determined spectrophotometrically as the thiourea complex, after decomposition and oxidation of the complexes as described by Roth and Hinckley.[11] Considerable difficulty was experienced in obtaining reproducible Os analyses, which appear to stem largely from the problems of quantitatively oxidising the Os to OsO_4 without loss (*cf.* ref. 11). The osmyl complexes were stored below 0 °C in the dark. $Cs_2[OsO_2X_4]$ (X = Cl or Br) were prepared by the method of Lott and Symons.[8]

$[OsO_2Cl_2(MeSCH_2CH_2SMe)]$.—A solution of OsO_4 (0.143 g, 0.56 mmol) in a mixture of ethanol (4 cm^3) and conc. hydrochloric acid (0.5 cm^3) was treated with $MeSCH_2CH_2SMe$ (0.062 g, 0.56 mmol) and the mixture stirred for 10 min, after which a light brown powder had deposited. This was collected, washed with H_2O (2 × 10 cm^3), ethanol (2 × 10 cm^3), and diethyl ether (3 × 10 cm^3), and dried *in vacuo* (0.13 g, 56%). The bromide was made similarly using conc. HBr.

$[OsO_2Cl_2\{o\text{-}C_6H_4(PPh_2)(SMe)\}]$.—To OsO_4 (0.5 mmol) in ethanol (3 cm^3) and conc. HCl (0.5 cm^3), was added the ligand (0.154 g, 0.5 mmol) in CH_2Cl_2 (2 cm^3). The mixture was stirred for 30 min, when an orange-brown solid was deposited. The CH_2Cl_2 was removed under reduced pressure, the solid collected and washed as described above (0.1 g, 36%).

The other complexes were generally prepared as described above for the 2,5-dithiahexane complex, those of the selenium ligands being prepared at 0 °C, and washed with cooled (< 0 °C) solvents to minimise decomposition. Analytical data are given in Table 2.

Acknowledgements

We thank the S.E.R.C. for support and for a postgraduate studentship (to S. K. H.), Mr. E. G. Hope for the sample of 2,5-diselenahexane, and Dr. M. Tajik for the data on $[OsO_2X_4]^{2-}$.

References

1 Part 13, H. C. Jewiss, W. Levason, M. Tajik, M. Webster, and N. Walker, preceding paper.
2 D. J. Gulliver, W. Levason, K. G. Smith, M. J. Selwood, and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1980, 1872.
3 R. Ali, S. J. Higgins and W. Levason, *Inorg. Chim. Acta*, 1984, **84**, 65.

4 For a review see D. J. Gulliver and W. Levason, *Coord. Chem. Rev.*, 1982, **46**, 1.
5 S. G. Murray and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 365.
6 J. E. Armstrong and R. A. Walton, *Inorg. Chem.*, 1983, **22**, 1545.
7 D. J. Salmon and R. A. Walton, *Inorg. Chem.*, 1978, **17**, 2379.
8 K. A. K. Lott and M. C. R. Symons, *J. Chem. Soc.*, 1960, 973.
9 D. Britnell, G. W. A. Fowles, and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 1975, 213.
10 P. M. Boorman, M. Islip, M. M. Reimer, and K. J. Reimer, *J. Chem. Soc., Dalton Trans.*, 1972, 891.
11 W. J. Roth and C. C. Hinckley, *Inorg. Chem.*, 1981, **20**, 2023.

Received 8*th May* 1984; *Paper* 4/735