Reaction of Tungsten(VI) Tetrachloride Sulphide and Selenide and the Analogous Bromides with a Range of Donor Molecules

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The compounds WX_4Y (Y = S and Se, X = Cl and Br) have been allowed to react with a range of ligands containing nitrogen, phosphorus, oxygen, and sulphur donor atoms. Simple six-co-ordinate adducts WX_4Y,L and $2WX_4Y$,L′ (L = unidentate and L′ = bidentate ligand) have been isolated in many cases and characterised. In these adducts the terminal W=Y bond is retained. Under more severe reaction conditions, longer reaction period or higher temperatures, tungsten can be reduced to the quinquevalent or quadrivalent state. Thus $MeSCH_2CH_2SMe$ (mte) gives WCl_3S,mte, while triphenylphosphine both reduces tungsten and extracts sulphur or selenium to give tungsten(IV) adducts of the type $WX_4,PPh_3,P(Y)Ph_3$.

WHEREAS the tungsten(VI) tetrahalide oxides WCl_4O and WBr_4O form simple adducts with such ligands as alkyl cyanides[1,2] and pyridine,[2] tungsten(VI) halides are readily reduced to lower oxidation states.[3-6] Hence the sexivalent state appears to be stabilised by the multiple tungsten–oxygen bond. Recently we have prepared the analogous sulphur and selenium compounds, WX_4S and WX_4Se (X = Cl and Br), which contain terminal tungsten–sulphur and –selenium bonds,[7,8] and studied their reactions with a range of ligands to see if these multiple bonds have a similar stabilising effect.

EXPERIMENTAL

The tungsten(VI) tetrahalide sulphides and selenides were prepared as described previously.[7,8] These compounds are very readily hydrolysed to give H_2S and H_2Se respectively, so their reactions were studied by conventional vacuum-line techniques. The compounds were analysed for bromine, chlorine, selenium, sulphur, and tungsten by standard titrimetric or gravimetric procedures; analytical data for all compounds are recorded in the Table.

(a) *Preparation of Complexes of* WCl_4S *and* WCl_4Se.—All the WCl_4Y preparations (Y = S or Se) were carried out in sealed ampoules at room temperature.

(i) WCl_4S,L *and* WCl_4Se,L [L = *methyl cyanide, pyridine* (*py*), *tetrahydrofuran* (*thf*), *and* 1,4-*oxathian* (*oxt*)]. The thio- or seleno-tungsten(VI) chloride (2 g) was allowed to react at room temperature with a slight excess of ligand (mol ratio 1 : 1·05) in the presence of dry benzene (100 cm^3). The resulting solutions were filtered on the vacuum line and the soluble *products* isolated by evaporation of the filtrate; this procedure was carried out as rapidly as possible since non-stoicheiometric products were formed from prolonged reactions or reaction at elevated temperatures.

(ii) $2WCl_4S$,L *and* $2WCl_4Se$,L [L = 1,4-*dioxan* (*diox*) *and* 1,2-*bis*(*methylthio*)*ethane* (*mte*)]. These compounds were prepared as for (a) (i) except that mol ratios of 1 : 0·53 were used.

(iii) WCl_4S,3*py*. This compound was obtained as a canary-yellow *precipitate* when neat py was allowed to react with WCl_4S for 1 week.

(iv) $WCl_4,PPh_3,P(S)Ph_3$ *and* $WCl_4,PPh_3,P(Se)Ph_3$. Reaction of WCl_4S or WCl_4Se with PPh_3 in a mol ratio of 1 : 5 for 1 week yielded bright yellow *solids* that were filtered off and washed with benzene.

(v) WCl_3S,*mte*. The compounds WCl_4S and mte were allowed to react in a 1 : 3 mol ratio in benzene solution; the red solution which formed initially subsequently deposited the product as an orange *solid*.

(vi) WCl_3S,*bipy*. The compound WCl_4S was fused with an excess of 2,2′-bipyridine at 190 °C for 3 h. The cold melt was extracted successively with benzene and dichloromethane to remove the excess of ligand, and the product remained as a red-brown *solid*. Reaction of stoicheiometric amounts of the thio- and seleno-halides with 2,2′-bipyridyl and 1,10-phenanthroline led to the formation of non-stoicheiometric products.

(b) *Preparation of Complexes of* WBr_4S *and* WBr_4Se.—The compounds WBr_4S and WBr_4Se are not sufficiently soluble in benzene to allow the preparation of complexes by mixing equimolar solutions of the thio- or seleno-halide and ligands. Accordingly all adducts were prepared by fitting a Soxhlet extraction device, the paper thimble being replaced by a glass sinter, to the vacuum line and extracting WBr_4S or WBr_4Se with a benzene solution of the ligand. Since each extraction cycle dissolved only a small amount of the halide, the latter was exposed initially to a large excess of the ligand.

(i) WBr_4S,L (L = MeCN *and oxt*), $2WBr_4S$,L (L = *diox*

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and mte), $2WBr_4Se$,*diox, and* $WBr_4,PPh_3,P(S)PPh_3$. The extraction procedure gave a red solution in each case from which the listed compounds precipitated; they were filtered and washed with benzene on the vacuum line.

(ii) '$WBr_4Se,2NCMe$' *and* '$WCl_4Se,2NCMe$.' Extraction of WBr_4Se with neat methyl cyanide gave a red solution which turned brown quite rapidly and deposited a brown *substance* whose analysis corresponded to $WBr_4Se,2NCMe$. When the red solution formed by extraction of WCl_4Se with $MeCN-C_6H_6$ solution was allowed to stand, a *product* whose analyses corresponded to $WCl_4Se,2NCMe$ was deposited.

Analytical data for the adducts

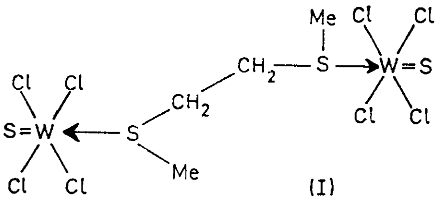
	Analyses/%																
	Found						Calc.										
Complex	W	Y[a]	X	C	H	N	W	Y[a]	X	C	H	N	Colour	*M*	μ/ B.M.	Oxidation state	Principal bands in i.r. spectra/cm⁻¹
WCl_4S,thf	42·9	7·6	33·3	10·7	1·9		42·8	7·4	33·0	11·2	1·9		Red	429	0·29	5·97	558s[b,c]
WCl_4Se,thf	38·3	16·3	29·4	10·1	1·9		38·6	16·6	29·8	10·1	1·7		Green		0·39	5·97	392s[b,c]
$2WCl_4S$,diox	45·8	7·7	35·2	6·2	1·3		45·8	8·0	35·3	6·0	1·0		Red	398[d]	0·38	5·95	560s[b,c]
$2WCl_4Se$,diox	40·7	18·8	31·5	6·2	1·4		41·0	17·6	31·6	5·3	0·9		Green		0·38	5·92	[e]
$2WBr_4W$,diox	31·0	5·1	55·3	4·4	1·2		31·7	5·5	55·2	4·1	0·7		Red		0·34		560s[b]
$2WBr_4Se$,diox	30·0	13·4	52·3	3·7	1·1		29·4	12·6	51·1	3·7	0·6				0·44		[e]
WCl_4S,oxt	39·5	6·3[f]	30·7	10·3	2·3		39·8	7·0[f]	30·7	10·4	1·7		Orange		0·56	5·99	553s[b,c]
WCl_4Se,oxt	36·0	14·4	27·6	10·5	1·8		36·0	15·5	28·6	9·4	1·6		Green-black		0·47	5·91	375m[b,c]
WBr_4S,oxt	28·5	4·6[f]	49·2	7·8	1·5		28·8	5·0[f]	50·0	7·5	1·1		Red		0·50		540m[b]
WCl_4S,NCMe	46·1	8·0	35·6	6·1	0·7	3·5	46·1	8·0	35·6	6·0	0·8	3·5	Red	437	0·35	5·93	550s[b,c]
WCl_4Se,NCMe	41·3	17·1	31·9	6·2	1·0	2·7	43·1	17·7	31·8	5·4	0·7	3·1	Green		0·44	5·90	390s[b,c]
$WCl_4Se,C_4H_6N_2$[g]	37·8	17·1	28·4	10·1	1·2	5·0	37·8	16·2	29·2	9·9	1·2	5·2	Red		1·82	4·00	435s, 425s, 325s, 310s, 280m
WBr_4S,NCMe	31·9	5·0	56·1	3·7	1·1	2·2	31·9	5·5	55·4	4·2	0·5	2·4	Red		0·60	5·90	545m[b]
$WBr_4Se,C_4H_6N_2$[g]	27·5	10·9	47·6	6·2	0·8	3·4	27·7	11·9	48·2	7·2	0·8	4·2	Brown		1·91	4·20	435s, 425s, 325s, 240m
WCl_4S,py	42·5	6·8	32·2	14·2	1·5	3·1	42·1	7·3	32·5	13·7	1·1	3·2	Orange		0·42	5·90	541s[b,c]
WCl_4S,3py[g]	30·6	6·0	23·6	30·6	2·9	7·0	30·9	5·5	23·8	30·4	2·5	7·1	Yellow		1·54		518s
WCl_4Se,py	38·4	15·9	29·8	11·9	1·4	2·5	38·0	16·3	29·3	12·4	1·0	2·9	Green-black		0·50	5·87	370s[b,c]
WBr_4S,2py	26·1	3·7	46·0	16·9	1·5	3·9	26·5	4·6	46·1	17·3	1·4	4·0	Yellow		0·43		[h]
WBr_4Se,2py	24·6	9·8	43·6	18·0	1·6	4·0	24·9	10·7	43·2	16·2	1·4	3·8			0·57		[e]
$WCl_4,PPh_3,P(S)Ph_3$	20·7		16·0	48·4	3·7		20·9		16·1	49·0	3·4		Yellow		1·70	4·1	600s [ν(P=S)],[h] 448w, 320s, 305s, 260w
$WCl_4,PPh_3,P(Se)Ph_3$	19·8		15·4	48·9	3·5		19·8		15·3	46·5	3·2		Yellow		1·98	4·0	[e,i]
$WCl_4,PPh_3,P(O)Ph_3$	21·0		15·9	50·1	3·8		21·2		16·4	49·9	3·5						1 150 [ν(P=O)][i]
$WBr_4,PPh_3,P(S)Ph_3$	17·8		30·9	40·5	2·8		17·4		30·2	40·8	2·8		Red		1·85	3·8	610s [ν(P=S)][h]
$2WCl_4S$,mte	44·1	7·2[f]	33·6	5·9	1·4		43·9	7·6[f]	33·9	5·7	1·2		Red		0·38		541s,[b] 380(sh), 345(sh), 330s, 290(sh), 260(sh)
WCl_3S,mte	41·1	6·9[f]	24·2	10·7	2·2		41·4	7·2[f]	24·0	10·8	2·2		Orange		1·45		535s,[b] 350s, 315s, 305s, 290m, 280m, 245w
$2WBr_4S$,mte	30·2	4·7[f]	53·8	5·4	1·5		30·8	5·4[f]	53·6	4·0	0·8		Red		0·32		525s[b]
WCl_3S,bipy	37·5	6·0	23·2	24·0	1·7	5·5	38·4	6·7	22·5	25·1	1·7	5·9	Red		1·52		531s,[b] 416, 340s, 326s, 253w, 240w, 233m

[a] Y = S or Se, X = Cl or Br. [b] ν(W=S) or ν(W=Se). [c] I.r. spectra assignable to metal–chlorine modes identical to those of $2WCl_4S$,mte. [d] Indicates dissociation of the species in solution. [e] ν(W=Se) was not observed. [f] Sulphur % calculated only to include sulphur in the thiohalide. [g] The exact nature of the compound is uncertain (see Discussion section). [h] ν(W=S) was not observed. [i] I.r. spectra assignable to metal–chlorine modes identical to those of $WCl_4,PPh_3,P(S)Ph_3$.

(iii) WBr_4S,*2py and* WBr_4Se,*2py*. These compounds precipitated as yellow *solids* from the red solutions formed initially by extraction with pyridine–benzene.

RESULTS AND DISCUSSION

(a) *Complexes with Sulphur Donors*.—The reactions of WX_4S (X = Cl and Br) with mte in a 1 : 0·5 mol ratio gave the isomorphous compounds $2WX_4S$,mte, and *X*-ray single-crystal studies have shown[9] that in each case two WX_4S units are linked by one molecule of ligand in the *trans*-form (I). The i.r. spectra (5 000—600 cm⁻¹) of these adducts exhibit the features expected for the *trans*-ligand.[10] Spectra for the 570—250 cm⁻¹ are given in the Table, and since the low-frequency spectra of all the tungsten(VI) adducts formed by $WSCl_4$ are much the same in this region, we suggest that the donor atom is *trans* to W=S in each case. There is a band at *ca.* 530 cm⁻¹ which may be attributed to ν(W=S), as we observed with the parent WX_4S compounds. When an excess of mte was used, reduction took place, with formation of the tungsten(V) compound WCl_3S,mte. The i.r. spectrum shows that the ligand is in a *gauche*-chelating form,[10] and a band at 535 cm⁻¹ indicates the presence of a terminal W=S bond; this band is missing from the spectrum of the parent WCl_3S, for which a W–S–W bridged structure (analogous to that of $NbCl_3O$) has been proposed.[8]



(I)

1,4-Oxathian gave 1 : 1 adducts in each case, and there was no evidence of reduction of tungsten to lower oxidation states. The i.r. spectra show that co-ordination of the ligand is only through the sulphur atom, since, while the C–S–C stretching frequencies of the ligand are modified in the adducts, there is no change in the C–O–C stretching frequencies.[11]

(b) *Complexes with Oxygen Donors*.—Both thf and 1,4-dioxan appear to form six-co-ordinate tungsten(VI) adducts. In each case the C–O–C stretching frequencies are modified in the usual way so that with diox we appear to have bridged adducts similar to $2WX_4S$,mte. Molecular-weight measurements show that WCl_4S,thf is monomeric in benzene solution, although the diox adduct appears to dissociate into WCl_4S and WCl_4S,diox; conductance measurements on these and the other 1 : 1 adducts show them to be non-electrolytes. The reaction procedure used for WBr_4S and WBr_4Se yielded

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only tarry products with thf, and it seems likely that oxygen may have been extracted from the ligand. We did not observe oxygen extraction from diox, however, although it is known [12] that under similar conditions WCl_4S reacts with 1,2-dimethoxyethane (dme) to give WCl_4S,WCl_2OS,dme, in which the two tungsten atoms are linked through the oxygen of the WCl_2OS unit.

(c) *Complexes with Nitrogen and Phosphorus Donors*.—The reactions of WX_4Y (Y = S and Se, X = Cl and Br) with nitrogen and phosphorus donors were fairly complicated, although under carefully controlled conditions simple 1 : 1 adducts were usually obtained. Reactions of methyl cyanide with WCl_4S, WBr_4S, and WCl_4Se gave WX_4Y,NCMe, and like the analogous WCl_4O,NCMe adduct [2] these compounds are monomeric non-electrolytes; the i.r. spectra show the expected change in ν(CN) on co-ordination. However, products of composition WCl_4Se,2NCMe and WBr_4Se,2NCMe were also obtained, and measurements of magnetic moment and oxidation state (by titration) clearly showed the tungsten to be in the quadrivalent state. The i.r. spectra show co-ordinated MeCN ligands to be present and bands that can be attributed to MeSeCN. Even though we could not isolate MeSeCN by careful hydrolysis, we feel that the adducts are likely to be WX_4,NCMe,NCSeMe, in which the selenium has been incorporated into one of the methyl cyanide molecules.

Analogous extraction of selenium (and sulphur) certainly does take place in reactions of triphenylphosphine with the WX_4Y compounds and in this respect we examined further the previously reported [2] reactions of WCl_4O and WBr_4O with PPh_3. For all the reactions, the analytical data corresponded to $WX_4Y,2PPh_3$, but the i.r. spectra and magnetic measurements show that the adducts should be considered as $WX_4,PPh_3,P(Y)Ph_3$. Thus the magnetic moments are consistent with tungsten(IV), and the absence of a ν(P–H) band eliminates the possibility of the adducts being of the type $[Ph_3HP]_2[WX_4Y]$; there are no ν(W=Y) (Y = O, S, or Se) bands, but typical $P(Y)Ph_3$ bands are present. Moreover, hydrolysis of the WCl_4O reaction product yielded a 1 : 1 mixture of PPh_3 and $P(O)Ph_3$; hydrolysis of the sulphur and selenium compounds also gave PPh_3 and $P(O)Ph_3$ in a 1 : 1 mixture, presumably because of hydrolysis of $P(S)Ph_3$ and $P(Se)Ph_3$.

Pyridine reacted with WCl_4S and WCl_4Se to give simple 1 : 1 adducts that were monomeric and non-conducting in solution, but the bromides WBr_4S and WBr_4Se gave 1 : 2 complexes (WBr_4Y,2py) as formed by WCl_4O.[2] Insolubility in suitable solvents precluded conductance and molecular-weight studies on the 1 : 2 complexes, but we tentatively suggest ionic structures $[WBr_3Y,2py]Br$. Reduction occurred when the py reactions were carried out at reflux temperature. With WCl_4S the product had the overall composition WCl_4S,3py and a magnetic moment of 1·54 B.M.,* which is a strong indication of tungsten(V), but we were unable to confirm this by the usual valence-state titration as the ligand interfered. In the analogous reduction by py of tungsten(VI) chloride 4-pyridylpyridinium chloride was formed,[6,13] and the i.r. spectrum of 'WCl_4S,3py' is not inconsistent with the formulation $[WCl_3S$,4-pyridylpyridinium]Cl, in which a terminal W=S bond remains.

Only non-stoicheiometric products resulted from room-temperature reactions of bipy with WX_4Y in 1 : 1 mol ratios, but reactions of WCl_4S with excess of fused bipy brought about reduction and formation of WCl_3S,bipy; the i.r. spectrum shows the expected ν(W=S) band, and the ν(W–Cl) modes are similar to those reported for WCl_3O,bipy.[14]

[4/1307 *Received*, 1*st July*, 1974]

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* 1 B.M. $\simeq 9{\cdot}27 \times 10^{-24}$ A m^2.

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