THE INORGANIC CHEMISTRY OF TUNGSTEN

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I. Introduction

The chemistry of tungsten is very varied, covering nine oxidation states from −2 to +6. The history of its development parallels that of inorganic chemistry itself and accurately reflects the various phases of the subject. Tungsten has been studied since the characterization of tungstic acid by

Woulffe (1779) and Scheele (1781). Oxychlorides were obtained by Wohler (1824) but were not recognized as such until more fully characterized by Riche (1857), who also prepared the pure hexachloride and hexabromide. The nineteenth century saw the development of the chemistry of the tungstates and halides and their derivatives. The early twentieth century workers, notably Lindner, Collenberg (alias Olsson), and Rosenheim, extended the aqueous solution chemistry by the preparation of anionic halide and cyanide complexes, but were able to obtain only two types of compound in which the metal had an oxidation state less than +4 (the dihalides and the salts of $W_2Cl_9^{3-}$). The preparation of derivatives of the lower oxidation states had to await the discovery of the hexacarbonyl (1928) and the cyclopentadienyl compounds (1954). In fact this division is almost complete, the earlier workers (pre-1930) producing mostly compounds of the high oxidation states and the more modern workers almost entirely of the lower oxidation states. With the more extensive use of nonaqueous solvents some interest is now being shown in the hydrolytically unstable complexes of the higher halides.

Despite its long and interesting history, the chemistry of tungsten has developed very unevenly. The paucity of tungsten(III) derivatives is particularly striking. The aim of this review is to summarize the known inorganic chemistry of tungsten, in the hope that the deficiencies will become more apparent.

Previous reviews have dealt with isopolytungstates (*157*), structures of the oxides (*13*, *130*), the carbonyls (*1*), and π-complexes (*89*, *98*, *124*, *129*, *237*, *289*). The treatment of these topics will be curtailed accordingly.

II. Halides, Oxyhalides, and Their Derivatives

Binary halides are now known for tungsten in all oxidation states from +2 to +6 inclusive, and very recently some halides with apparent fractional oxidation states have been reported. Oxyhalides are restricted, with one exception, to tungsten(VI).* The simple halides and their derivatives by substitution will be discussed first, followed by the complex anions and adducts. Some properties of the halides and oxyhalides are summarized in Table I.

A. HALIDES AND OXYHALIDES

1. Tungsten(VI)

The three hexahalides—fluoride, chloride, and bromide—are volatile, diamagnetic solids or liquids, but the hexabromide is unstable to loss of

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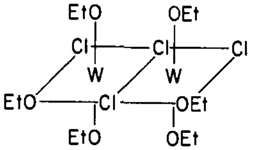
* See Section II, A., *2*, p. 319.

TABLE I
Some Properties of Tungsten Halides and Oxyhalides

	Compound	Trouton constant (e.u.)	$-\Delta H_f$ (kcal/mole) (*287*)	μ_{eff} (B.M./W atom)
WF_6	Colorless gas	21.8 (*205*)	416 (*205*)	diamag.
WCl_6	Steel blue, volatile solid	25.0 (*160*)	97	diamag.
WBr_6	Unstable, dark blue solid		44	diamag.
WF_5Cl	Unstable, yellow liquid		—	
WCl_5	Green, volatile solid	22.8 (*259*)	82	1.1
WBr_5	Black, volatile solid	23.1 (*259*)	43	1.0
WF_4	Red-brown, involatile solid		—	
WCl_4	Black, involatile solid		69	diamag.
WBr_4	Black, involatile solid		35	diamag.
WI_4	Black, involatile solid		0.5	
WBr_3	—		—	0.45
WI_3	—		—	ca. 4
WCl_2	Gray, involatile solid		36	diamag.
WBr_2	Yellow-gray, involatile solid		18.7	
WI_2	Brown, involatile solid		1	
WOF_4	White, volatile solid	31.0 (*259*)	—	
$WOCl_4$	Scarlet, volatile solid	33.2 (*259*)	178	
$WOBr_4$	Brown-black, volatile solid		—	
WO_2Cl_2	Unstable yellow, volatile solid		200	

bromine, giving the pentabromide. The hexahalides form regular octahedral molecules, as has been demonstrated by infrared and Raman (*45, 112, 278*), ^{19}F nmr (*46, 201*), and ^{35}Cl nqr (*131, 262*) spectroscopy and by X-ray (*159*) and electron (*37, 81*) diffraction. Reaction of tungsten hexafluoride with titanium tetrachloride gives a volatile chloropentafluoride, WF_5Cl, together with other unidentified chlorofluorides. The ^{19}F nmr and infrared spectra of the chloropentafluoride are compatible with an octahedral structure (*58*).

Ammonolysis of tungsten hexachloride gives products in which one or two chlorine atoms are replaced by NH_2 groups, $WCl_5NH_2{\cdot}2NH_3$ and $WCl_4(NH_2)_2{\cdot}2NH_3$; on heating, both these products give $WCl_2(NH)_2$ (*99*). Aminolysis with primary amines, however, yields tetraamido derivatives $WCl_2(NHR)_4$. The use of secondary or tertiary amines leads to reduction, giving $WCl_6^{=}$ which may then be aminolyzed, for example to $WCl_3NR_2{\cdot}2NHR_2$ (*38*). Alcoholysis also leads to reduction, to the blue, paramagnetic trichloroalkoxides, $WCl_3(OR)_2$ ($R = Me, Et$). The ethyl compound undergoes further solvolysis to yield the red, diamagnetic dimer $W_2Cl_4(OEt)_6$ formulated as (I) on the basis of the ^{1}H nmr spectrum and the dipole moment (*167*). The green compound obtained by Fischer and



(I)

Michiels (*85*) by electroreduction of tungsten hexachloride in ethanol is now thought to be a tungsten(IV) derivative, $W_2Cl_4(OEt)_4 \cdot 2EtOH$ (*167*). Phenolysis of the hexachloride is also possible, to give the tetra- and hexaphenoxides, $WCl_2(OAr)_4$ and $W(OAr)_6$ (*101*, *228*). Hexaphenoxides have also been obtained by the reaction of phenols with tungsten oxytetrachloride (*199*). These compounds are stable to hydrolysis and undergo phenol exchange in acid conditions. The rings may be brominated or nitrated without cleavage of the W—OC bonds (*199*). With dinitrogen pentoxide in carbon tetrachloride, tungsten hexachloride gives the volatile, highly reactive nitrato compound $WO_2(NO_3)_2$ (*250*).

Tungsten hexafluoride does not undergo substitution reactions with amines, the adducts being stable (*54*). With sulfur trioxide a product formulated as $WF_2(SO_3F)_4$ is obtained (*54*).

Oxyhalides are of two types: WOX_4 and WO_2X_2 ($X =$ F, Cl, Br). A dioxydifluoride was claimed in 1907 but has never been mentioned since (*243*). The structure of neither type of oxyhalide is known, although preliminary crystallographic data have been reported (*168*). In the gas phase, WO_2X_2 would be expected to be tetrahedral, like $MoOCl_2$ (*285*). The insolubility of solid WO_2Cl_2 and its high Trouton constant suggest that the compound is polymeric. Similar considerations suggest that the oxytetrachloride is also associated in the condensed phases. For other MOX_4 systems, both oxygen bridging and halogen bridging have been suggested [see below and reference (*277*)]. In solution the W=O stretching frequency is normal (Table II, p. 000). This frequency could not be located for the solid, but for molybdenum oxytetrachloride there is a reduction in frequency from 1003 cm^{-1} (CS_2) to 958 cm^{-1} (solid) (*79*).

Infrared and mass spectroscopic measurements show that the dioxydihalides are monomeric in the gas phase. The mass spectrum shows a low concentration of a dimeric species, which also occurs in solution. The dimers must be halogen bridged, since W=O stretching frequencies are observed at about 980 cm^{-1}. For the solid, these frequencies do not appear and new bands are found at 750–800 cm^{-1}, suggesting polymerization through oxygen bridges (*20a*).

On heating to 200°–300°C, the dioxydihalides disproportionate into the trioxide and the oxytetrahalides.

Substitution of the chlorine atoms in the oxytetrachloride to give compounds of the type $WO(OR)_4$ has been achieved with a wide variety of alcohols (*108*), phenols (*230*), and carboxylic acids (*231*). The alkoxy derivatives may be hydrolyzed to polytungstates (*148*). Partial substitution is also possible, to give $WOCl_3(OR)$ (*106*).

Oxide ligands, such as triphenylphosphine oxide or pyridine *N*-oxide, will react with tungsten oxytetrachloride or the hexachloride to give oxygenated products of the type $WO_2Cl_2L_2$ (L = Ph_3PO, Me_2SO, C_5H_5NO) (*84*). Similar compounds have been obtained by the atmospheric hydrolysis of the products of halogenation of bis(tertiary-phosphine)tungsten tetracarbonyls (*177*).

2. Tungsten(V)

The only pentahalides known are the chloride and bromide. The pentafluoride may well be unstable to disproportionation like those of molybdenum, rhenium, and osmium (*47*), a process which would be favored by the high heat of formation of tungsten hexafluoride ($\Delta F°_{298} = -397$ kcal/mole) (*205*).

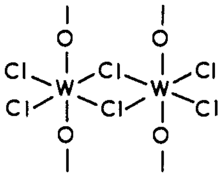
The structures of the pentahalides are not known, but are presumably similar to that of molybdenum pentachloride. In the vapor phase, molybdenum pentachloride consists of trigonal bipyramidal molecules (*81*), which dimerize in the solid (*245*). There is some evidence for dimerization of the tungsten compounds in the vapor phase, but the heat of dissociation is small and the Trouton constant normal (*257*). The magnetic moments of the solid pentahalides are low, 1.0–1.1 B.M., but independent of temperature (*270*) (cf. $MoCl_5$: $\mu_{eff} = 1.67$ B.M., also temperature-independent) (*65*). Low values could arise from spin-orbit coupling or from metal-metal interaction, but the moment might then be expected to be temperature-dependent in both cases. The temperature independence has recently been confirmed by Colton and Tomkins (*64*), who pointed out that the magnetic moment corresponds to one third of an unpaired electron per tungsten atom. They suggested a trimeric structure, $[W_3X_{12}]X_3$, analogous to that of the rhenium(III) clusters.

Substitution of two or three halogen atoms may be achieved directly with phenols (*107*). The substitution of the third halogen atom is difficult, and completely substituted compounds, $W(OAr)_5$, have been obtained only by reduction of the hexaphenoxides (*105*).

No oxyhalides of tungsten(V) were known until very recently, but a phase of composition $WO_2 \cdot WCl_6$ appears in the WO_2/WCl_6 phase diagram (*258*).

Tungsten(V) oxytrichloride, $WOCl_3$, has now been prepared by aluminium reduction of the oxytetrachloride. It is virtually diamagnetic

($\chi'_M = 60 \times 10^{-6}$ c.g.s.). The infrared spectrum and X-ray powder pattern suggest that the structure is analogous to that of $NbOCl_3$ (*98a*)



This structure is similar to that proposed for solid WO_2Cl_2 (see p. 318), which is obtained by replacing the bridging chlorine atoms by oxygen atoms.

3. Tungsten(IV)

Tetrahalides are known for all four halogens. They are dark, involatile, insoluble, diamagnetic solids, isomorphous with the corresponding niobium and tantalum tetrahalides (*43*). The latter compounds have structures in which MX_6 octahedra form linear chains by sharing edges. The diamagnetism arises through metal-metal bonds, which draw the metal atoms together in pairs (*248*).

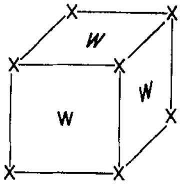
The thermal stabilities of the tungsten tetrahalides are very dependent on the halogen. The tetraiodide is unstable to loss of iodine even at room temperature. The tetrabromide and tetrachloride disproportionate into the penta- and dihalides on heating to 450°–500°C; this is a very convenient way of obtaining pure samples of these halides. The tetrahalides themselves are best prepared by reduction of the higher halides with aluminum in a controlled temperature gradient (*43*). A bromotrichloride, obtained by the action of bromine on $K_3W_2Cl_9$, is reported, surprisingly, to sublime in nitrogen at 135°C (*293*).

Tungsten tetrafluoride is obtained by reduction of the hexafluoride with benzene at 110°C (*233*). A similar method has been used to prepare molybdenum tetrachloride from the pentachloride (*171*), but tungsten hexachloride is not reduced at 80°C (*127*). The tetrafluoride has surprisingly high thermal stability, being unaffected up to about 800°C, above which temperature it dissociates into its elements (*234*).

The only known oxyhalide of tungsten(IV) is the oxydifluoride, WOF_2, obtained by the action of hydrogen fluoride on tungsten dioxide at 500°C. It, too, is extremely inert (*234*).

4. Lower Halides

Until very recently (1962) the only lower tungsten halides known were the dihalides—chloride, bromide, and iodide. These, like the molybdenum dihalides (*42*), are hexanuclear, containing the $W_6X_8^{4+}$ unit (*265*). This cluster may be envisaged as a cube of halogen atoms with a tungsten atom situated at the center of each of the cube faces (II). The cubes are linked together in a two-dimensional lattice by bridging halogen atoms, the remaining two halogen atoms being situated above and below the cube, giving a $[W_6X_8]X_2X_{4/2}$ arrangement. Each tungsten atom is thus coordinated to a square pyramid of halogen atoms and is also bound to four other tungsten atoms, which are coplanar. The molecular orbital scheme for the $M_6X_8^{4+}$ cluster shows that these compounds should be diamagnetic, as observed (*70*).



(II)

The tungsten dihalides are markedly less stable than those of molybdenum, in that they are oxidized even by water (*179*). There is also a considerable difference in the ease with which substitution of the halogen atoms may be effected. To convert Mo_6Cl_{12} to Mo_6Br_{12} requires fusion in lithium bromide (*261*), whereas the corresponding conversion for the tungsten compound can apparently be achieved merely by warming with hydrobromic acid (*179*).

If W_6Br_{12} is allowed to react with liquid bromine at temperatures up to 110°C, an unstable tribromide is formed (*43*, *182*, *265*). At 140°C an intermediate bromide of composition $WBr_{2.67}$ is obtained; this material is also produced by heating the tribromide under the same conditions. Above 160°C, both these compounds are oxidized to the hexabromide. Both WBr_3 and $WBr_{2.67}$ are unstable to loss of bromine, and on heating in a vacuum give a further bromide, $WBr_{2.33}$. The latter material has not been obtained directly from W_6Br_{12}. All these bromides revert to the W_6Br_{12} on strong heating (*265*). The ease with which these compounds are interconverted suggests that the W_6 unit is retained throughout the series, which is then formulated: W_6Br_{12}, W_6Br_{14}, W_6Br_{16}, W_6Br_{18}. The interrelations are shown in Fig. 1. This hexanuclear structure has been shown for W_6Br_{16}, in which $[W_6Br_8]Br_4$ units are linked in chains by linear Br_4^- ions (*249*). This behavior parallels that of the niobium and tantalum halides, $[M_6X_{12}]X_2$, which undergo two-electron oxidations without breakdown of the cluster (*183*). M_6X_8 clusters are also found in Ta_6I_{11} (*249*).

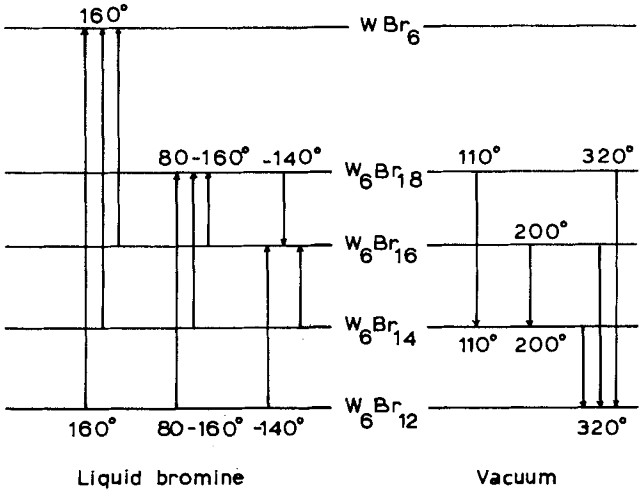


FIG. 1. Interconversions of the hexanuclear tungsten bromides [after Siepmann and Schäfer (*265*)].

Magnetic data are available only for W_6Br_{18}, which is antiferromagnetic with a Néel temperature above 355°K. The moment is low, being at room temperature 1.1 B.M. per W_6 unit (*43*). In marked contrast, the magnetic moment of WI_3 (which compound is obtained by reaction of tungsten hexacarbonyl with iodine at 120°C) is about 4 B.M. at room temperature and is field-dependent (*77*). The triiodide loses iodine on standing and reverts to the diiodide, W_6I_{12}. No trichloride has yet been reported.

These trihalides are thus very different from the molybdenum trihalides, which are stable to dissociation but unstable to disproportionation into the pentahalide and Mo_6X_{12} (200°–400°C). These trihalides have TiI_3-type chain structures (bromide, iodide) (*17*, *174*) or $CrCl_3$-type layer lattices (chloride) (*254*), both of which involve simple MoX_6 groups, although in the trichloride the metal atoms form pairs. These compounds are also antiferromagnetic (*174*, *248*).

5. *Thermodynamics*

Thermodynamic data are available from many sources (*19*, *46*, *201*, *256*, *259*, *260*, *287*). For the halides the Russian enthalpy values are considerably higher than the American values, although there is agreement in the entropies. The relationship between the halides is shown in Fig. 2. The high stability of the hexafluoride and the instability of the hexabromide and the iodides are clearly shown. Tungsten pentachloride appears to be unstable to disproportionation at room temperature, but there is no evidence that such a reaction occurs. On raising the temperature the hexachloride

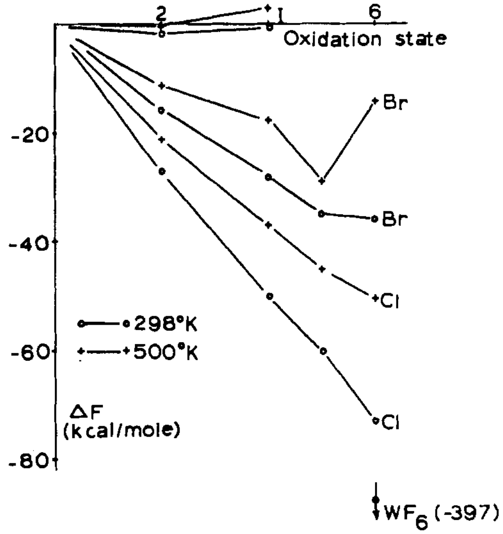


FIG. 2. Free energies of formation of tungsten halides at 298° and 500°K [data from (*287*)].

TABLE II

INFRARED DATA FOR HALIDE AND OXYHALIDE DERIVATIVES[a]

Compound	ν_{M-X}	δ_{M-X}	ν_{M-O}	δ_{M-O}	Ref.
$WOCl_4$ (CS_2)			1030		(*79*)
($SOCl_2$)			1019		(*65*)
$WO_2Cl_2(OPPh_3)_2$			960, 913		(*177*)
$WO_2Cl_2(dpO_2)$			956, 909		
$WO_2Br_2(dpO_2)$			954, 907		
Et_4NWCl_6	329				(*4*)
	305				(*18*)
Me_4NWCl_6	315				
Rb_2WOCl_5	339, 317	177, 164	930	229	(*244*)
Cs_2WOCl_5	333, 309	174, 164	957	230	
Rb_2WOBr_5	224	142, 120	968	203	
Cs_2WOBr_5	220	143, 119	960	202	
K_2WCl_6	324	164			(*5*)
Rb_2WCl_6	306	160			
Cs_2WCl_6	308	166			
K_2WBr_6	229	74			
Rb_2WBr_6	220	78			
Cs_2WBr_6	214	60			

[a] All values are in cm^{-1}; $dpO_2 = Ph_2P(O)CH_2CH_2P(O)Ph_2$.

TABLE III
COMPLEXES OF TUNGSTEN HALIDES AND OXYHALIDES[a]

$[WO_2F_4]^{=}$	(*31*)	$WF_6 \cdot ArH$	(*233*)	$[WO_3Cl]^{-}$	(*235*)	$WOCl_4 \cdot 4RNH_2$	(*229*)		
$[WO_3F_3]^{3-}$	(*251*)	$WF_6 \cdot 3L$ (L = py, $MeNH_2$)	(*54*)	$[WO_2Cl_3]^{-}$	(*63*)	$WO_2Cl_2 \cdot 3NH_3$	(*267*)		
$[WO_3F_2 \cdot H_2O]^{=}$	(*252*)			$WCl_6 \cdot$diars	(*55*)	$WO_2Cl_2L_2$ (L = Ph_3PO, Me_2SO, C_5H_5NO diphosO_2)	(*84,177*)		
$[WO_4F]^{3-}$	(*253*)	$WF_6 \cdot 4NH_3$	(*54*)	$WCl_6 \cdot 6L$ (L = NH_3, $ArNH_2$)	(*99,227*)				
$[WF_8]^{=}$	(*21,72, 132*)	$WOF_4 \cdot SeF_4$	(*22*)						
$[WF_7]^{-}$	(*114, 132*)	$WOF_4 \cdot SeOF_4$	(*22*)	$WCl_6 \cdot 4NH_3$	(*99*)				
$[WOF_5]^{-}$	(*132, 204*)			$WOCl_4L$ (L = Et_2O, Me_2CO, RCN, bipy, 2py)	(*106*)				
$[WF_6]^{-}$	(*133, 155*)			$[WCl_6]^{-}$	(*4,18*)	$[WCl_4bipy]Cl$	(*127*)	$[WOBr_5]^{=}$	(*223*)
				$[WOCl_5]^{=}$	(*63,59*)	$WCl_5 \cdot PCl_5$	(*128*)	$[WOBr_4]^{-}$	
$[WF_8]^{-}$	(*132*)			$[WOCl_4]^{-}$				$[WOBr_4 \cdot H_2O]^{-}$	
				$[WOCl_4 \cdot H_2O]^{-}$				$WBr_5 \cdot 5RNH_2$	(*232*)
				$[WCl_6]^{=}$	(*5,38,155*)	WCl_4L_2 (L = py, RCN, diphos)	(*10,43,127, 157*)	$[WBr_6]^{=}$	(*156*)
				$[W(OH)Cl_5]^{=}$	(*62,170*)			WBr_4L_2 (L = py, RCN)	(*10,43, 156*)
				$WCl_4 \cdot S_4N_4$	(*75,209*)				
				$[W_3Cl_9]^{3-}$	(*62*)			$[W_3Br_9]^{3-}$	(*292*)
				$W_2Cl_6L_3$ (L = $PhNH_2$, py)	(*36,152*)				
				$[W_6Cl_{14}]^{=}$	(*142,179*)			$[W_6Br_{14}]^{=}$	(*142*)
				$W_6Cl_{12} \cdot 2EtOH$	(*203*)				

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[a] py = pyridine, bipy = bipyridyl, diars = o-$C_6H_4(AsMe_2)_2$, diphos = $Ph_2PC_2H_4PPh_2$, diphosO_2 = $Ph_2P(O)C_2H_4P(O)Ph_2$.

and tetrachloride become relatively less stable, with the effect of stabilizing the pentachloride against disproportionation, and it is now the tetrachloride which is unstable with respect to decomposition into the dichloride and pentachloride.

B. Complex Anions and Adducts

Large numbers of anionic halide and oxyhalide complexes are known, mostly for tungsten(V); this has been one of the major areas of study in the chemistry of tungsten. The other adducts have been only poorly characterized. The known complexes are summarized in Table III.

1. Tungsten(VI)

A variety of oxyfluoride anions is known, some at least of which contain octahedrally coordinated tungsten. This has been shown for $[WOF_5]^-$ (*132*), $[WO_2F_4]^=$ (*143*), and $[WO_3F_3]^{3-}$ (*251*). The fluoride and oxide ions have similar radii (1.36 and 1.40 Å, respectively) and are probably distributed randomly (*222*).

Salts of the octafluorotungstate(VI) anion, $[WF_8]^=$, have been reported as being formed by the reaction of alkali fluorides with tungsten hexafluoride (*132*), but it was later shown that no reaction occurs if the alkali fluoride is perfectly dry (*72*). These salts are best obtained by the reaction of the hexafluoride with an alkali iodide in iodine pentafluoride (*132*). Nitrosyl fluoride similarly gives $(NO)_2WF_8$, which is isomorphous with the corresponding rhenium compound (*2*). In the alkali salts M_2ReF_8, the anions have a square antiprismatic configuration (*27*), which may be retained in the nitrosyl compound.

If an excess of tungsten hexafluoride is used in these reactions, cubic heptafluoro complexes, MWF_7, are obtained (*132*). Similarly, alkali and tetraethylammonium chlorides dissolve in phosphorus oxychloride solutions of tungsten hexachloride to give heptachlorotungstate(VI) ions (*16*).

The structures of the other adducts and of the oxyhalides are not known.

2. Tungsten(V)

The anionic complexes of tungsten(V) are all octahedral, with the possible exceptions of $[WF_8]^{3-}$ (*132*) and $[WOX_4]^-$ (X = Cl, Br, I).

Salts of composition MWX_6 are known for X = F, Cl, Br. The fluorides are obtained from alkali iodides and tungsten hexafluoride in liquid sulfur dioxide (*155*). The chloro and bromo complexes are prepared either by reduction of the hexahalide, with an iodide at about 100°C (*76*) or with thionyl chloride (*4, 18*), or by direct addition of a chloride or bromide to the corresponding pentahalide in an inert solvent (*39, 40, 76*). The fluoro compounds are isomorphous with the corresponding hexafluoroantimonates(V), $MSbF_6$ (*155*); the anions are therefore octahedral, with possibly a slight trigonal distortion for the cesium and rubidium salts and a definite tetragonal distortion for the potassium salt. The structure of the hexachlorotungstates(V) is not known, but the observation of a single W—Cl stretching frequency (see Table II) is indicative of octahedral coordination (*4*, *18*).

All the hexahalogenotungstate(V) salts have low magnetic moments, 0.5–1.3 B.M. at room temperature, and the fluoro and chloro complexes are antiferromagnetic with Néel temperatures of 100°–150°K (Table IV).

TABLE IV
MAGNETIC PROPERTIES OF HEXAHALOGENOTUNGSTATES(V)

Compound	μ_{eff} (B.M., ca. 300°K)	Néel temperature (°K)	Ref.
$NaWF_6$	0.52	130	
KWF_6	0.53	ca. 125	
$RbWF_6$	0.58	110	(*133*)
$CsWF_6$	0.59	ca. 100	
$NaWCl_6$	0.88^a		
$KWCl_6$	ca. $0.9^{a,b}$		
$RbWCl_6$	ca. $0.9^{a,b}$		(*76*)
$CsWCl_6$	ca. $1.1^{a,b}$		
$CsWCl_6$	0.95	105	
Me_4NWCl_6	1.23	100	(*18*)
Et_4NWCl_6	0.64	140	
Et_4NWCl_6	0.66^a		(*76*)
Ph_4AsWCl_6	1.21^a		
Et_4NWBr_6	1.28^a		(*40*)
Et_3NHWBr_6	1.23^a		

[a] Measured at room temperature only.

[b] Values varied for different preparations.

The antiferromagnetism presumably arises by exchange coupling through the halide ions, as in K_2IrCl_6.

The colors of the salts are governed by charge-transfer bands, the fluorides being white, the chlorides green, and the bromides very dark green or black. The ligand-field bands probably occur at about 27,000 cm^{-1} (chloride) and 15,000–19,000 cm^{-1} (bromide) (Table V).

With the exception of the lithium salt, the fluoro complexes are stable up to 250°C (*155*), but the chlorides disproportionate at this temperature

TABLE V
Electronic Spectra of Tungsten Complexes (*147*)

	Absorption bands (cm^{-1})					
Anion	Ligand-field		Charge-transfer			
WCl_6^-	27,400		32,260	35,700	39,200	42,800
WBr_6^-	14,900	18,900	23,500			
$WCl_6^{=}$	19,230		31,750	35,300	39,400	42,600
$WBr_6^{=}$	20,100	25,200	33,000			
$WOCl_5^{=}$	14,200	25,190	32,790	37,170		
$WOBr_5^{=}$	14,290		25,640			
$MoOCl_5^{=}$	14,100	22,420	28,010	32,260	40,000	
$MoOBr_5^{=}$	14,290	21,280	24,100	26,530		

into tungsten hexachloride and the hexachlorotungstates(IV). This reaction may be reversed by grinding the tungsten(IV) compound with the hexachloride (*76*).

When a solution of a tungstate in concentrated hydrochloric acid is reduced, chemically or electrolytically, an intensely blue solution is obtained from which several types of complex may be precipitated. The stoichiometry of the product seems to depend only on the precipitant: alkali chlorides give green M_2WOCl_5, quinoline or pyridine gives brown $(AmH)WOCl_4$, while tetraalkylammonium chlorides give the light blue $R_4NWOCl_4 \cdot H_2O$ (*59, 63*). A similar series of bromo complexes results from reduction in hydrobromic acid and addition of the appropriate precipitant (*223*).

A molecular orbital scheme has been proposed (*122*) for the MO^{2+} systems in which significant π-bonding is restricted to the M=O bonds (Fig. 3). This scheme accounts satisfactorily for the major features of the absorption spectra of the $[MOCl_5]^{=}$ ions (M = Mo, W; X = Cl, Br) (see Table V) (*9*). Thus the first *d-d* transition ($^2B_2 \rightarrow {}^2E$, $b_2 \rightarrow e_\pi^*$) occurs at about 14,000 cm^{-1} for all the complexes, and there is a blue shift of about 4000 cm^{-1} in the second band ($^2B_2 \rightarrow {}^2B_1$) on going from the molybdenum complexes to those of tungsten. Charge transfer from ligand to metal is indicated by a similar blue shift (ca. 5000 cm^{-1}) in the charge-transfer bands, but there is a shift in the opposite direction (ca. 4000 cm^{-1}) on changing the halide from chloride to bromide. This has been interpreted as implying the involvement of the halide π-system, which would be of higher energy than that of oxygen and would therefore be involved in the lowest charge-transfer transitions (*147*).

The magnetic susceptibilities follow the Curie-Weiss law in the range 90°–300°K with small values of θ (Table VI) (*9*). The asymmetry of the

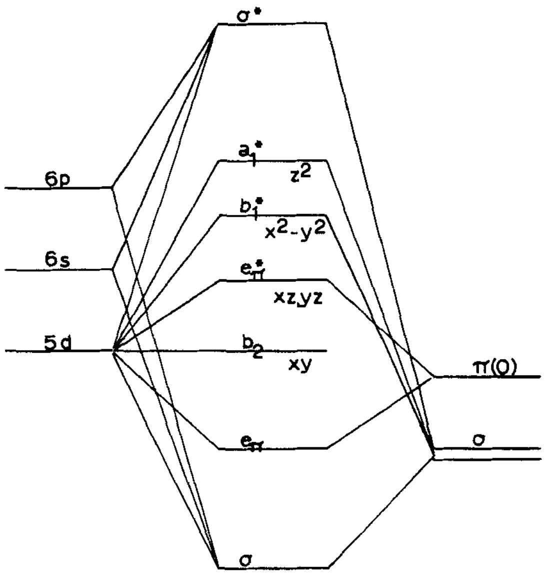


FIG. 3. Molecular orbital scheme for $[MOX_5]^-$ [after Gray and Hare (*122*)].

metal environment effectively quenches the orbital contribution ($^2B_2$ ground state) and the π-bonding results in a considerable diminution of the spin-orbit coupling constant; nevertheless the magnetic moments are appreciably below the spin-only value.

For the $[WOX_4]^-$ salts, the magnetic moments and θ values are similar to those for $WOX_5^=$ (Table VI). The absorption spectra of $[WOX_4]^-$ have not been reported, but those of the corresponding molybdenum complexes

TABLE VI

MAGNETIC PROPERTIES OF TUNGSTEN(V) OXYHALIDE COMPLEXES (*9*)

Complex	μ_{eff} (B.M., ca. 300°K)	θ (°K)
Rb_2WOCl_5	1.55	20
Cs_2WOCl_5	1.49	16
$Me_3NHWOCl_5$	1.35	4
Rb_2WOBr_5	1.37[a]	—
Cs_2WOBr_5	1.55	17
quinH $WOCl_4$	1.41	6
pyH $WOCl_4$	1.43[a]	—
quinH $WOBr_4$	1.40[a]	—
isoquinH $WOBr_4$	1.37[a]	—

[a] Measured at room temperature only.

show marked differences between measurements made on solutions (in liquid sulfur dioxide) and on the solid complexes, the frequency of the first ligand-field band being lower in the solid. It has been suggested that octahedral coordination of the metal is achieved either by solvation or by oxygen bridging. The latter effect would weaken the M═O π-bonding and lead to a decrease in frequency of the first *d-d* band (*9*). Dimerization by halogen bridging has also been postulated (*11*).

Although the presence of water in $[WOCl_4, H_2O]^-$ has never been explicitly demonstrated, these compounds differ markedly from the anhydrous ones both in color and in ease of hydrolysis.

The only other adducts of tungsten pentahalides appear to be $[WCl_4bipy]Cl$ (*127*), $WCl_5{\cdot}PCl_5$ (*128*) ($[PCl_4]^+ [WCl_6]^-$?), and $[W(amine)_5Br_3]Br_2$ (*232*).

3. Tungsten(IV)

The only well-substantiated anionic complexes of tungsten(IV) are the hexahalogenotungstates(IV), $[WX_6]^=$ (X = Cl, Br, I), obtained by heating the higher tungsten halides with an alkali iodide (*76*, *156*). The reaction proceeds by initial formation of the tungsten(V) complexes (see above). The tungsten(IV) chloro compounds also appear as intermediates in the aminolysis of tungsten hexachloride (*38*). The alkali salts have cubic, K_2PtCl_6 structures; the anions are therefore octahedral, with the exception of the potassium salt which is tetragonally distorted (*156*). The distortion is not enough to give a splitting of the ^{37}Cl nqr spectrum (*206*). This salt shows a higher W—Cl stretching frequency than the cubic rubidium and cesium salts (Table II), although this difference has also been attributed to metal-ligand π-bonding (*5*). The values for the bromo compounds decrease more regularly. The magnetic moments of the salts are low and the θ values high (Table VII), suggesting antiferromagnetism; a Néel point was observed for K_2WCl_6 at 80°K (*156*).

These salts react with pyridine to give complexes of the type WX_4py_2 (X = Cl, Br) (*156*), which may also be obtained by direct reaction of pyridine with the tetra-, penta-, or hexahalides (*43*). The reduction proceeds with the formation of the 1-(4-pyridyl)pyridinium ion (*43*). Similar complexes are obtained with other heterocyclic amines (*43*) and with nitriles (*9*). The X-ray patterns of these derivatives are complicated, but the pyridine complexes are isomorphous with those of niobium and tantalum (*43*). The magnetic moments are again depressed, although less markedly than for the $WX_6^=$ salts (Table VII). The majority of these compounds are soluble only in the parent ligand to give nonconducting solutions (*9*), although the conductivity of the pyridine complexes in pyridine slowly increases, with accompanying changes in the absorption

TABLE VII
MAGNETIC PROPERTIES OF TUNGSTEN(IV) DERIVATIVES

Derivative	μ_{eff} (B.M., ca. 300°K)	θ (°K)	Reference
K_2WCl_6	1.43	180	(*5*)
Rb_2WCl_6	1.47	160	
Cs_2WCl_6	1.47	122	
Tl_2WCl_6	1.76	375	
$BaWCl_6$	0.89	400	
K_2WBr_6	1.42	200	
Rb_2WBr_6	1.42	137	
Cs_2WBr_6	1.72	148	
WCl_4py_2	2.06	(antiferro)	(*156*)
	1.6		(*43*)
WBr_4py_2	2.03	180	(*156*)
	2.1		(*43*)
$WCl_4(MeCN)_2$	1.78		(*9*)
$WCl_4(EtCN)_2$	1.84		
$WCl_4(Pr^nCN)_2$	1.85		
$WBr_4(MeCN)_2$	1.89		
$WBr_4(EtCN)_2$	1.85		
$WBr_4(Pr^nCN)_2$	2.07		

spectrum, suggesting that further addition is possible (*43*). A molecular weight determination could be made only on the propyl cyanide derivative, which is monomeric in freezing benzene (*9*). The observation of two C≡N and two M—Cl stretching frequencies in $MoCl_4(MeCN)_2$ may be indicative of a *cis* octahedral configuration (*9*).

If a hydrochloric acid solution of a tungstate is reduced beyond the tungsten(V) stage, a dark red paramagnetic complex may be isolated, analyzing as $K_2W(OH)Cl_5$ (*62*). This compound apparently contains tungsten(IV) and the magnetic moment, 2.2 B.M. at room temperature (*270*), is not incompatible with this oxidation state. However, polarographic studies have shown that reduction occurs directly from tungsten(V) to tungsten(III), with no evidence for the intermediate tungsten(IV) stage (*180*). The complex has an intense absorption band in the visible region (19,900 cm^{-1}, $\epsilon_{mol} > 10^4$) (*170*), which may indicate a binuclear complex with tungsten atoms in two different oxidation states. In solution the complex decomposes rapidly, but is stabilized by high concentrations of chloride ions. One major product of the decomposition is $[W_2Cl_9]^{3-}$, which has been taken to imply a disproportionation mechanism (*170*).

4. Tungsten(III)

The ultimate products of the reduction of tungstates in hydrohalic acid solution are the diamagnetic ions $[W_2X_9]^{3-}$ [X = Cl, green (*62, 215*), Br, brown (*292*)]. In these anions each tungsten atom is octahedrally surrounded by six halide ions, the two octahedra having a common face. The tungsten atoms are displaced slightly from the centers of the octahedra, forming a short tungsten-tungsten bond of length 2.41 Å (cf. 2.74 Å in the metal) (*41, 283*). The absorption spectrum shows two bands in the visible region, at 13,200 cm^{-1} (ϵ_{mol} ca. 25) and 16,300 cm^{-1} (ϵ_{mol} ca. 400). These bands were attributed to spin-forbidden transitions (*154*), but it is more likely that they are spin-allowed *d-d* transitions between the orbitals of the metal-metal bond system.

Similar complexes exist for molybdenum, but no details have been published (*173*). There are no tungsten complexes corresponding to the readily prepared hexahalogenomolybdates(III), MoX_6^{3-} (X = Cl, Br, I). The preparation of $KWF_4{\cdot}9H_2O$ has been briefly reported (*241*).

Chloride exchange studies on $W_2Cl_9^{3-}$ suggest that complete exchange of all nine halide ions occurs (*134*). However, attempts to substitute the chloride with bromide or iodide lead to decomposition of the complex, with production of $WO_2{\cdot}xH_2O$ (*120*). Similar oxidation occurs when the chloro complex is allowed to stand in water or alkali (*292*). The dimeric anion probably dissociates and is then oxidized by the solvent.

The salt $K_3W_2Cl_9$ reacts with refluxing pyridine or aniline to give brown, diamagnetic complexes $W_2Cl_6L_3$ (*152*). The same products may be obtained more conveniently by pyrolysis of, for example, $(pyH)_3W_2Cl_9$ (*36*). The structures of these compounds are not known.

It has been suggested, on the basis of chloride exchange and spectroscopic studies, that other tungsten(III) species may exist in solution, but their nature is unknown (*180*). The reported "red tungsten(III)" (*180*) and the compound $K_5W_3Cl_{14}$ (*172*) both appear to contain $[W(OH)Cl_5]^{=}$ (*170*).

5. Tungsten(II)

The $[W_6X_8]^{4+}$ group probably always has six ligands coordinated to it, as in the solid dihalides (*265*), $[W_6Br_8]Br_4\,(EtOH)_2$ (*203*), and the many salts of $[W_6X_8]X_6^{=}$ (*142, 179*).

The only known simple complex of tungsten(II) appears to be $W(diars)_2I_2$ (diars = *o*-phenylenebisdimethylarsine), which has a magnetic moment of 2.70 B.M. (20°C) and is isomorphous with its molybdenum analog (*77*). All other monomeric tungsten(II) complexes involve carbonyl or aromatic ligands and contain seven-coordinate, diamagnetic tungsten (see Section VI).

III. Cyano Complexes

The major class of tungsten cyano complexes is that of the octacyanotungstates(IV and V). Until recently these were the only known tungsten complexes containing cyanide ligands only, but complexes of tungsten(II and III) are now known.

A. OCTACYANOTUNGSTATES AND THEIR DERIVATIVES

The octacyano complexes of molybdenum and tungsten are so similar in all respects (except properties such as oxidation potentials) that they may be discussed jointly and data for either may be applied to both. In this way a large body of information is available.

The $[M(CN)_8]^{4-}$ ions are obtained by reaction with aqueous cyanide ion of many other complexes containing the tri-, quadri-, or quinquevalent metal, e.g. halides (*15, 44, 117, 137, 214, 215, 236, 239, 292*), oxalates (*20, 59*), thiocyanates (*240*), hydroxides (*192*). Trivalent metal is oxidized by either the solvent or the atmosphere, while the pentavalent starting materials disproportionate, the other product being $[MO_4]^{2-}$ (*292*). It does not appear possible to obtain $[M(CN)_8]^{3-}$ directly, but only by oxidation of the quadrivalent complex. This oxidation occurs, as expected, more readily for tungsten than for molybdenum (*61*). The quadrivalent compounds are diamagnetic (d^2) (*15, 32, 238*), and the quinquevalent compounds show paramagnetism corresponding to a single unpaired electron (μ_{eff} = 1.76 B.M. (W), d^1) (*15*).

Until recently the structure of these ions was not known with any certainty. An X-ray examination of $K_4[Mo(CN)_8]\cdot 2H_2O$ (with which the corresponding tungsten salt is isomorphous (*15*)) showed a slightly distorted dodecahedral configuration for the anion (*144*). However, the Raman spectrum of an aqueous solution of this salt appeared to be consistent with a square antiprismatic configuration (*268*). Stammreich and Sala took existing infrared data (*141*) and suggested that this configuration was maintained in the solid state. Other infrared spectra appeared to agree with neither the antiprismatic nor the dodecahedral structure (*35, 82, 181*). High resolution work has now clarified the situation for the solid, for which the spectrum is entirely consistent with the distorted dodecahedral structure found by X-ray examination (*161, 217*). The infrared spectra of salts with other cations are also consistent with a more or less distorted dodecahedral configuration (*217*).

Further refinement of the original X-ray data suggests that the distortion of the anion from D_{2d} symmetry is not very great and that the M—CN bonds all have a similar length (*145*). In a dodecahedral structure four of the CN groups are better placed than the other four for π-bonding (with the $d_{x^2-y^2}$ orbital on the metal), and the ligand replacement reactions have been explained on this basis (*216*). Hoard and Silverton suggest that the bond shortening which such π-bonding would produce is offset by inhomogeneous repulsion due to the electron pair in $d_{x^2-y^2}$. However, such repulsions would be quite small since this orbital has its maxima between the ligands. This must mean that the π-bonding is weak and that the shape of the complex is determined by interligand repulsions and σ-bond strengths (*145, 158, 219*). Electron delocalization in $Mo(CN)_8^{3-}$ is very small (see below).

For solutions, the position is less clear. The ^{13}C nmr spectrum of $[Mo(CN)_8]^{4-}$ consists of a single line, which implies either that the groups are all very similar (antiprism) or that there is rapid intramolecular mixing of CN groups (*200*). (Intermolecular exchange may be ruled out since exchange with CN^- does not occur—see below.) It has been suggested that interconversions between dodecahedral and antiprismatic configurations could occur readily (*145*). The effect on the nmr spectrum of a decrease in temperature was not examined. The infrared spectra of aqueous solutions consist of a single, very broad line, in marked contrast to the spectrum of the solid. Such broadening could be caused, for example, by vibration or solvation of the anion, but the Raman spectrum does not appear to be unduly broadened (*268*). Cooling to −60°C had no effect on the infrared spectrum (*161, 217*). The electronic spectrum has been interpreted in terms of both models (*169, 224*). This spectrum, however, is very similar to the diffuse reflectance spectrum of the solid (*169*) and it seems unlikely that the actual configuration in solution is very different from that in the solid.

Oxidation of $[M(CN)_8]^{4-}$ (for example with permanganate) gives the quinquevalent complexes which are stable in the absence of light. Little is known of the structure of these ions. The electronic spectra have been interpreted in terms of both dodecahedral and square antiprismatic configurations (*169, 224*). The esr spectrum has recently been redetermined. From the relative values of $g_{||}$ and $g_\perp$ it was concluded that the anion had a square antiprismatic structure in solution but became dodecahedral when co-crystallized with $K_4M(CN)_8{\cdot}2H_2O$ (*186*). Analysis of the fine structure of the spectrum obtained with $[Mo(^{13}CN)_8]^{4-}$ gave a spin density on the metal atom of 0.96, showing that π-delocalization is small (*284*).

Both the $[M(CN)_8]^{4-}$ and $[M(CN)_8]^{3-}$ ions are stable in solution in the dark and no exchange with $^{14}CN^-$ can be detected in either case (*7, 15, 117*). For $[M(CN)_8]^{4-}$ this exchange is strongly photocatalyzed, the rate being dependent on the light intensity (*7*). The half-life of the reaction is independent of concentration, showing that the rate-determining step involves the photoexcited species (*117*). Ligand replacement reactions are similarly photoinduced although the detailed mechanism of these reactions is not clear. If the yellow solutions of $[M(CN)_8]^{4-}$ are exposed to light in the range 300–500 mμ, the color changes rapidly to red and then, more slowly, to violet (W) or blue (Mo) (*49, 60, 150*); these colors are due to the ions $[M(CN)_4(OH)_3H_2O]^{3-}$ (*150, 178, 193*). The color changes are accompanied by an increase in pH of the solution (*7, 185*). If the reaction is stopped at the red stage and the solution is allowed to stand in the dark or is heated, the yellow color is regained and the pH decreases (*7, 151, 185*). The color reversal can also be achieved by addition of base (*150, 151*). Adamson and Perumareddi have shown that the red color develops maximum intensity most rapidly at high light intensities and that there is concurrent production of free CN^-, approximately one g-ion of CN^- per g-ion of photolyzed complex (*6*). The rate of disappearance of the red color, after irradiation, is dependent on the concentration of CN^-, an excess of which also inhibits the formation of the final blue product. It is suggested that the red intermediate is $[M(CN)_7(OH)]^{4-}$, which may undergo thermal reactions either experiencing further (presumably stepwise) substitution or returning to $[M(CN)_8]^{4-}$ by reaction with CN^- or HCN (*6*). Similar conclusions were reached by Carassiti and his co-workers (*49*). The reversal of the yellow-red reaction by base suggests that CN^- is the reagent.

Jakob *et al.* find that in the presence of a base (e.g., NH_3, N_2H_4) the reaction does not proceed beyond the red stage and is no longer reversible (*150, 151*). From this solution red salts can be isolated, such as $Cd_2W(CN)_8 \cdot 2NH_3$, and it is claimed that the two molecules of base are associated with the anion, even in solution (*149–151*). It is suggested that the $[M(CN)_8]^{4-}$ ion undergoes a change of configuration from dodecahedral to antiprismatic and that the two "extra" ligands are bound to the two square faces. Such an arrangement would be favored by polarizable ligands, the square faces being regions of negative charge density. Water molecules, being less polarizable than those of amines, would be bound less strongly, accounting for the greater lability of this system (*151*). Jakob further suggests that this is the initial stage in the photohydrolysis reaction, but it is difficult to see why the addition of other bases or of cyanide should reverse this stage if no substitution is occurring.

The $[M(CN)_8]^{3-}$ ions are also stable, in the dark, to CN^- exchange, hydrolysis, and reduction. On exposure to light, reduction occurs rather than solvolysis, and a chain mechanism involving OH radicals has been proposed to explain the observation of quantum yields greater than unity (*48*). By contrast, electron exchange between $[M(CN)_8]^{3-}$ and $[M(CN)_8]^{4-}$ is very fast, even in the dark (*118*).

As mentioned above, the ultimate product of photohydrolysis is

$[M(CN)_4(OH)_3(H_2O)]^{3-}$. It is only possible to isolate tetrasubstituted species; an early report (*60*) of $[M(CN)_5(OH)_3]^{4-}$ has been shown to be incorrect (*30, 48, 151*). The form of the tetrasubstituted complex is dependent on the acidity of the medium, three protonation stages being possible before decomposition (*178*), e.g.,

$$\underset{\textit{brown-yellow}}{[W(CN)_4(OH)_4]^{4-}} \rightleftharpoons \underset{\textit{lilac}}{[W(CN)_4(OH)_3(H_2O)]^{3-}} \rightleftharpoons \underset{\textit{blue}}{[W(CN)_4(OH)_2(H_2O)_2]^{2-}} \xrightarrow[T>60^\circ]{H^+} \underset{\textit{green}}{W(CN)_2(OH)_2}$$

Salts of each of the anions have been isolated (*178*). The color changes are due to a red shift in a ligand-field band as protonation proceeds. For example, the diffuse reflectance spectra of the potassium salts show maxima at 21,000 cm^{-1} for $[W(CN)_4(OH)_4]^{4-}$ and 19,100 cm^{-1} for $[W(CN)_4(OH)_3(H_2O)]^{3-}$ (*218*). This shift is the opposite of that expected from the spectrochemical series and the "average environment" rule. These complexes undergo a reversible one-electron oxidation and the oxidation potential has been measured (*195*). The heats of combustion (*194*) and acidity constants have also been reported (*178*).

If the salts $Ag_4[M(CN)_8]$ are allowed to react with alkyl iodides (methyl, ethyl, *t*-butyl, triphenylmethyl, allyl), reaction again occurs at four sites to give $M(CN)_4(CNR)_4$ (*146, 220*). The visible spectra of the solutions of these compounds are very similar to that of the parent ion, and they presumably have the same dodecahedral structure. An early report suggests that it may be possible to obtain ionic species containing only two alkyl groups (*146*).

B. CYANOTUNGSTATES(II AND III)

The reduction of anhydrous $K_4M(CN)_8$ with hydrogen at 330°–390°C gives green or black products which analyze as $K_4M(CN)_6$. Oxidation state determinations support their formulation as derivatives of the bivalent metals. Extraction of these products with methanol in the presence of air yields yellow-brown solids of composition $K_3M(CN)_6$. The conductivities of solutions of these compounds are consistent with the presence of $M(CN)_6^{3-}$ and $M(CN)_6^{4-}$ ions. The solutions are very reducing and on standing develop a yellow color, presumably due to $[M(CN)_8]^{4-}$. The infrared spectra of the solids are complex, suggesting nonoctahedral structures, which is also indicated by the magnetic data [magnetic moments (B.M.) at room temperature: $K_4M(CN)_6$, 1.13 (Mo), 0.94 (W); $K_3M(CN)_6$, 1.50 (Mo), 1.76 (W) (*166*)].

C. CARBONYLCYANO COMPLEXES

Cyanide ion may replace CO in $W(CO)_6$, when up to three CN groups may be coordinated giving $[W(CO)_{6-n}(CN)_n]^{n-}$, in which the CN groups are mutually *cis* (*24*, *25*). The complexes $[\pi\text{-CpW}^{\text{II}}(\text{CO})_3\text{CN}]$ and $[\pi\text{-CpW}(\text{CO})_2(\text{CN})_2]^-$ and their methyl derivatives $[\pi\text{-CpW}(\text{CO})_n\text{-}(\text{CNCH}_3)_{4-n}]$ have been obtained (*56*).

IV. Thiocyanato Complexes

Many thiocyanato complexes are known, mostly for tungsten(V) (cf. the halides). The majority of these complexes are not well characterized, but it appears that the NCS group coordinates through nitrogen.

A. TUNGSTEN(VI)

Solutions of WCl_6, WOCl_4, or WO_2Cl_2 in acetone or similar solvents react with thiocyanate ion to give the substituted products W(NCS)_6, WO(NCS)_4, and $\text{WO}_2(\text{NCS})_2$, but these have never been obtained free of solvent, there usually being 2 moles of solvent per mole of compound, e.g. $\text{W(NCS)}_6 \cdot 2(\text{CH}_3)_2\text{CO}$ (*103*).

Neutral or weakly acid aqueous solutions of tungstates react with thiocyanate to give condensed tungstates or thiocyanatotungstates, both of which are colorless (*33*). No further data have been reported.

B. TUNGSTEN(V)

Despite their long use in analysis (*83*), the nature of the colored species obtained by reduction of tungstate with thiocyanic acid has only recently been elucidated. The stoichiometry of these complexes is markedly dependent on the acidity of the solutions, and the following sequence of equilibria has been suggested on the basis of the amine salts which can be isolated (*33*, *102*):

$$\underset{\text{(III) } \textit{red-brown}}{[\text{WO(OH)}_2(\text{NCS})_2]^-} + \text{NCS}^- \rightleftharpoons \underset{\text{(IV) } \textit{brown}}{[\text{WO}_2(\text{NCS})_3]^{2-}} + \text{H}_2\text{O}$$

$$\underset{\text{(IV)}}{[\text{WO}_2(\text{NCS})_3]^{2-}} + \text{H}^+ + \text{NCS}^- \rightleftharpoons \underset{\text{(V)}}{[\text{WO(OH)(NCS)}_4]^{2-}}$$

$$\underset{\text{(V)}}{[\text{WO(OH)(NCS)}_4]^{2-}} + \text{H}^+ \rightleftharpoons \underset{\text{(VI) } \textit{violet}}{[\text{WO(NCS)}_4]^-} + \text{H}_2\text{O}$$

$$\underset{\text{(V)}}{2[\text{WO(OH)(NCS)}_4]^{2-}} \rightleftharpoons \underset{\text{(VII) } \textit{orange-brown}}{[\text{W}_2\text{O}_3(\text{NCS})_8]^{4-}} + \text{H}_2\text{O}$$

$$\underset{\text{(VII)}}{[\text{W}_2\text{O}_3(\text{NCS})_8]^{4-}} + 2\text{H}^+ \rightleftharpoons \underset{\text{(VIII) } \textit{green}}{2[\text{WO(NCS)}_5]^-}$$

Anions (III), (IV), (VI), (VII), (VIII), and $[\text{W(OH)}_3(\text{NCS})_3]^-$ (IX) (dark violet) give amine salts with the colors shown. No salt of (IV) appears to have been isolated.

Nothing is known of the structures of most of these complexes, but (VI) and (VIII) are presumably analogous to the corresponding halogeno complexes. It has been suggested that the molybdenum complex corresponding to (IV) is dimeric, $[Mo_2O_4(NCS)_6]^{4-}$, with a double oxygen bridge (*196*, *197*). Infrared measurements on salts of (III) and (IX) are consistent with coordination of the thiocyanate through nitrogen [$\nu_{C-N} = 2058$ cm^{-1} (IX) (*101*); $\nu_{C-S} = 815$ cm^{-1} (III) (*33*),] and this may reasonably be assumed for the remainder. The spectrum of (III) also shows the presence of hydroxyl groups and indicates extensive hydrogen bonding (*33*). The position of the W=O stretching frequency was not recorded.

Complex (VIII), $[WO(NCS)_5]^-$, is paramagnetic (no value given) and (VII), $[W_2O_3(NCS)_8]^{4-}$, is diamagnetic (*33*). The latter presumably has a single oxygen bridge through which the unpaired electrons are coupled.

The species which is extracted into organic solvents from acidic aqueous solutions has been assigned the formula $[W(NCS)_2X_4]^-$, where X was shown not to be halide (*8*). This complex must presumably be (III), $[WO(OH)_2(NCS)_2]^-$, although other compositions have been suggested (*119*, *225*). The complex $py_2WO_2(NCS)_3$ (*240*) is probably the pyridinium salt of (IV), although the color is different from that of Böhland's product (*102*).

C. TUNGSTEN(III)

Olsson found that reaction of aqueous $K_3W_2Cl_9$ with thiocyanic acid gave a deep red color which could be extracted into ether. This extract yielded a red oil which was found to contain tungsten(III) but was not further characterized (*213*). Böhland has also obtained evidence for reduction to tungsten(III) by polarography in methanol (*33*). No such complexes have yet been isolated (cf. $Mo(NCS)_6^{3-}$).

D. TUNGSTEN(0)

A thiocyanato analog of $[W(CO)_5Hal]^-$ has been obtained by reaction of $W(CO)_6$ with $(CH_3)_4NNCS$ in diglyme. The product is a yellow solid with moderate air stability. The infrared spectrum shows C_{4v} symmetry and bonding of the NCS group through nitrogen ($\nu_{C-S} = 791$ cm^{-1}). Similar compounds have been isolated from $Cr(CO)_6$ and $Mo(CO)_6$ but the molybdenum compound is unstable (*291*).

V. Oxides and Tungstates

A. OXIDES

Tungsten trioxide has a slightly distorted ReO_3-type structure in which WO_6 octahedra are linked in three dimensions by sharing corners in a $WO_{6/2}$ arrangement (*130*). The dioxide has a deformed rutile structure, in which the WO_6 units are linked in chains by common edges, the chains being bound into two-dimensional layers by sharing the apical oxygens. Within the individual chains, the tungsten atoms are drawn together in pairs, alternate tungsten-tungsten distances being 2.49 and 3.08 Å (cf. 2.74 Å in the metal) (*130*). The dioxide is diamagnetic (*264*).

Several substoichiometric oxides also exist. When the trioxide is heated strongly *in vacuo*, oxygen is lost preferentially, giving a defect lattice. This process continues to a limiting composition of $WO_{2.98}$, beyond which several new phases begin to appear (*113*). These phases consist of blocks of the basic ReO_3-type structure separated by shear planes or dislocations (*110, 113, 130*). In well-annealed samples the shear planes are parallel and regularly spaced, giving phases of well-defined but complex stoichiometry. Where the ReO_3 blocks are separated by shear planes, phases of composition W_nO_{3n-1} are obtained, where *n* is a measure of the thickness of the block (*130*). The known phases are $W_{50}O_{148}$, $W_{40}O_{118}$, $W_{25}O_{74}$, $W_{20}O_{58}$, $W_{18}O_{49}$, and W_4O_8. In samples prepared at low temperatures (less than 1000°C) the shear planes occur randomly (*109*).

When the trioxide vaporizes, polymeric species are formed, which have been detected mass spectrometrically. The major species are W_4O_{12}, W_3O_9, W_3O_8, and W_2O_6 (*3*). The free energies of formation of these species and of the solids $W_{18}O_{49}$, $W_{20}O_{58}$, and $W_{50}O_{148}$ have been measured (*3, 211*).

The hydrated forms of the trioxide, the so-called tungstic acid, appear to contain only lattice water. Infrared and ^1H nmr studies gave no evidence of hydroxyl groups (*255*). However, the volatility of tungsten trioxide increases considerably in the presence of water vapor, owing to the formation of $WO_2(OH)_2$ (*115*).

B. TUNGSTATES

The oxo anions of tungsten(VI) range from the simple $WO_4^{=}$ tetrahedra and WO_6^{6-} octahedra (*271*) to highly polymeric species such as $W_{24}O_{72}(OH)_{12}^{12-}$ (*116*). These isopolytungstates consist of WO_6 octahedra linked by common corners, although in the early members WO_4 tetrahedra may also occur.

The chemistry of the isopolytungstates has been reviewed (*157*); more recent data are given by Aveston (*14*) and Glemser *et al.* (*116*).

VI. Aromatic and Carbonyl Complexes

The lowest oxidation states of tungsten, as of other metals, are stabilized by ligands which can accept electrons from the metal by π-back-donation. Outstanding among these ligands is carbon monoxide, which occurs in complexes in which tungsten has oxidation states of −2 to +3; tungsten hexacarbonyl has the highest metal—CO bond energy of those measured to date. Unsaturated organic molecules, and aromatic systems in particular, are also effective electron acceptors; the cyclopentadienyl anion, for instance, forms complexes in which the formal oxidation state of the tungsten is in the range +1 to +5.

Complexes of both these types have recently been reviewed (*1*, *89*, *124*, *129*, *140*, *289*); the present discussion will be condensed accordingly. Since both types of ligand frequently occur in the same complex and stabilize much the same oxidation states with similar stereochemistries, it is convenient to treat both together.

To facilitate discussion, oxidation states and coordination numbers will be assigned using the formalisms that radical ligands act as the corresponding anions and organic groups donate all their π-electron "pairs" to the metal. Thus in cyclopentadienyl complexes the ligand is formally "tridentate" $C_5H_5^-$, so that $[\pi\text{-}C_5H_5W(CO)_3]_2$ would be a derivative of seven-coordinate tungsten(I).

A. TUNGSTEN(−II AND −I)

Carbon monoxide provides the only complexes in which tungsten has a negative oxidation state, in the anions $[W(CO_5)]^{=}$, $[W_2(CO)_{10}]^{=}$, $[W_2(CO)_9]^{4-}$, and $[W_3(CO)_{14}]^{=}$ (*23*, *25*, *26*). The structure of none of these is known with certainty, but $[W(CO)_5]^{=}$ is presumably trigonal bipyramidal. The infrared spectrum of $[W_2(CO)_{10}]^{=}$ in the C=O stretching region (*140*) is compatible with a staggered structure as in the isoelectronic $Re_2(CO)_{10}$ (*73*). A protonated derivative, $[W_2(CO)_{10}H]^-$, has been described (*25*), the nmr and infrared spectra of which suggest that the hydrogen atom is bound equally to both metal atoms and that the D_{4d} symmetry is maintained (*12*).

B. TUNGSTEN(0)

Tungsten(0) occurs not only in the hexacarbonyl, $W(CO)_6$, and its multitudinous substitution products, but also in dibenzenetungsten, $(\pi\text{-}C_6H_6)_2W$ (*97*), hexakisisonitriletungsten, $(RNC)_6W$ (*138*, *188*), and tris(1,2-bisdiphenylphosphinoethane)tungsten, $(Ph_2PC_2H_4PPh_2)_3W$ (*53*). All these compounds are diamagnetic and contain six-coordinate tungsten. Thermodynamic data are available only for the hexacarbonyl, which shows the solid tungsten compound to be slightly less stable than its chromium and molybdenum analogs, although the mean bond dissociation energies for the process

$$\tfrac{1}{6}M(CO)_{6(g)} \rightarrow \tfrac{1}{6}M_{(g)} + CO_{(g)}$$

increase regularly (Cr, 27.1; Mo, 35.9; W, 42.1 kcal/bond) (*69*). The lower heat of formation of $W(CO)_6$ is presumably due mainly to the high heat of atomization of the metal (220 kcal/g-atom). A compound of composition $(bipy)_3W$ is paramagnetic ($\mu_{eff} = 1.03$, 20°C) (*138*, *139*) and may therefore not be a true tungsten(0) derivative.

The stability and ease of handling of tungsten hexacarbonyl (as of those of chromium and molybdenum) have made it the object of much study. In particular, the substitution reactions have been extensively investigated with ligands of all types; introductory references may be obtained from Abel's review (*1*). The types of reaction may be summarized as follows:

(*i*) Reaction with 1 mole (or less) of a monodentate ligand at 100°–160°C gives monosubstitution.

(*ii*) Reaction with 2 moles of a monodentate ligand or 1 mole of a bidentate ligand at 100°–160°C results in disubstitution.

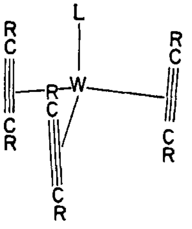
Both these reactions may be carried out at room temperature under ultraviolet radiation (*273*, *276*), when reaction apparently occurs via an unstable pentacarbonyl, $W(CO)_5$. The infrared spectrum of this intermediate suggests that it has a square pyramidal configuration at −180°C. The corresponding molybdenum species apparently isomerizes to a trigonal bipyramidal form above −155°C (*274*).

(*iii*) Reaction with excess ligand at higher temperature (180°–240°C) gives trisubstitution. These derivatives can often be obtained more conveniently from the intermediates $(CH_3CN)_3W(CO)_3$ (*280*) or (π-mesitylene)-$W(CO)_3$ (*96*).

(*iv*) Substitution of more than three CO groups is difficult and has been achieved only with bidentate ligands at high temperatures. All the ligands used to date are capable of π-bonding with the metal (*24*, *52*, *210*).

Derivatives in which more than one CO group is replaced are usually obtained in the *cis* form; the *trans* complexes are seldom obtainable pure. This is consistent with the theory of M—CO π-bonding. The major exception to this rule appears to be the trisubstituted acrylonitrile complex. In the mono- and disubstituted complexes the ligand is bound to the metal through the nitrogen atom, $(CH_2{:}CHCN{\rightarrow})_nW(CO)_{6-n}$ ($n = 1, 2$), while in the tricarbonyl coordination apparently occurs via the double bond and the complex is obtained entirely in the *trans* form (*191*, *242*). This complex is also of interest since it is one of the few derivatives in which a mono-olefin is bound to the metal by its double bond. A few other unstable compounds are known (*273*), but olefin coordination normally requires chelation as with dienes, aromatic systems, or in $(o\text{-}Ph_2As{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH_3)W(CO)_4$ (*28*).

Reaction of $W(CO)_6$ or $(CH_3CN)_3W(CO)_3$ with acetylenes results in the formation of $(RC{\vdots}CR)_3W(CO)$ (R = ethyl (*279*), phenyl (*275*)), or $(CF_3C{\vdots}CCF_3)_3W(CH_3CN)$ (*165*), in which it is suggested that the four groups are situated tetrahedrally around the metal atom (X) (*279*).



(X)

σ-Bonded derivatives $K_3[(RC{:}C)_3W(CO)_3]$ may be obtained by reaction of $(NH_3)_3W(CO)_3$ with the potassium alkynyl in liquid ammonia (*207*). The action of ethereal LiR on $W(CO)_6$ gives $[W(CO)_5COR]^-$ (R = Me, Ph) (*93*).

The high symmetry of the Group VI hexacarbonyls has made them the object of much theoretical discussion (*121, 153*). In particular, the force constants of the C═O stretching vibrations have been correlated with the degree of M—CO π-bonding. It has recently been suggested that in $M(CO)_6$ the three nonbonding electron pairs on the metal are fully utilized in π-bonding. The M—C bond order would then be 1.5, rising to 2.0 when three of the CO groups are replaced with ligands which are incapable of π-bonding (*68*). This seems unrealistic in view of the fact that π-bonding is expected to increase in the isoelectronic series $[Mn(CO)_6]^+$, $Cr(CO)_6$, $[V(CO)_6]^-$ (*78*). Also, the π^* orbitals of CO, into which the metal electrons are donated, are probably of higher energy that the t_{2g} orbitals of the metal, and figures of 0.1 and 0.2 electron pair transferred per CO group have been proposed (*78, 121*).

C. TUNGSTEN(I)

There are only two monomeric representatives of tungsten(I): $[(C_6H_6)_2W]^+$ (*97*) and $[(diphos)_2W(CO)_2]I_3$ (diphos = $Ph_2PCH_2CH_2PPh_2$) (*176*). The single unpaired electron gives magnetic moments of 1.58 and 1.86 B.M., respectively.

The phosphine compound is remarkable in that the two CO groups are apparently *trans*. It has been suggested (*176*) that this configuration is adopted for steric reasons, which may also inhibit the dimerization expected for a low-valent heavy metal complex with an odd number of electrons. All other formal tungsten(I) derivatives are dimeric, and diamagnetic.

Treatment of tetramethyldiphosphine or -diarsine with $W(CO)_6$ gives the diamagnetic complexes $(CO)_5W(LMe_2)_2W(CO)_5$ (L = P, As) (*50, 51, 136*). The small dipole moment (ca. 1 D) of these compounds has been interpreted in terms of folding about the L—L axis, which would enhance the metal-metal bond (*51*), but the nmr spectra suggest that the four

TABLE VIII
X Groups Reported for π-CpW(CO)$_3$X

X Group	References
π-CpW(CO)$_3$	(*91,288,290*)
H, Me, Et	(*91,226*)
σ-CH$_2$:CH$_2$CH$_2$-, σ-Me$_2$CH-, π-CH$_2$:CHCH$_3$	(*125*)
CF$_3$-, C$_3$F$_7$-, σ-CH$_2$:CH-	(*164*)
σ-CHF$_2$CF$_2$-	(*281*)
π-CH$_2$:CH$_2$	(*57*)
C$_2$H$_5$CO—	(*184*)
CO	(*88,90*)
NO	(*86*)
Halogen	(*87*)
Cl$_3$Sn-	(*34*)
PhSnCl$_2$-, Ph$_3$Sn-, Ph$_3$Pb-, [π-CpW(CO)$_3$]SnPh$_2$-, [π-CpW(CO)$_3$]SnCl$_2$- [π-CpW(CO)$_3$]PbPh$_2$-, [π-CpW(CO)$_3$]PbCl$_2$-	(*208*)
[Mn(CO)$_5$]SnMe$_2$-	(*221*)
Ph$_3$PAu-	(*57*)
NH$_3$, N$_2$H$_4$	(*94*)
Other compounds:	
π-CpW(CO)$_2$(π-C$_3$H$_5$)	(*125*)
[π-CpW(CO)$_2$SMe$_2$]$_2$	(*135,281*)
π-CpW(CO)(Hal)(π-Ph$_4$C$_4$)	(*187*)
[π-CpW(π-C$_6$H$_6$)CO]$^+$	(*90*)

methyl groups are all equivalent, implying a planar WL$_2$W system (*136*).

In [π-CpW(CO)$_3$]$_2$ (Cp = cyclopentadienyl, C$_5$H$_5$) two π-CpW(CO)$_3$ groups are held together by a single, long (3.28 Å) tungsten-tungsten bond. The molecule has a center of symmetry and the axis of the ring is coincident with that of the W(CO)$_3$ system (*290*).

D. Tungsten(II)

Several tungsten(II) compounds are known, all of which are diamagnetic and seven-coordinate. Of these, approximately half are of the type π-CpW(CO)$_3$X. The X groups reported to date are listed in Table VIII. It may reasonably be presumed that the structures of these complexes are analogous to that of [π-CpW(CO)$_3$]$_2$, the group X replacing one π-Cp(CO)$_3$W unit.

The remaining tungsten(II) compounds have all been obtained by the halogenation of substituted carbonyls. Except for [(diphos)$_2$W(CO)$_2$]$^+$ (see above) (*176*), smooth, two-electron oxidations occur. Reaction usually takes place without loss of carbon monoxide to give seven-coordinate complexes in which one halide ion is coordinated and the other is ionic, the compounds being uniunivalent electrolytes. In other cases, 1 mole of carbon monoxide is lost during the oxidation and nonelectrolytes are obtained (Table IX). This is probably the more stable form, since [(v-triars)W$(CO)_3$X]X is converted to [(v-triars)W$(CO)_2X_2$] by heating to 200°C (*212*). With the corresponding molybdenum complexes this conversion is easier (*66*, *212*) and the nonelectrolytes are more often obtained directly (*66*, *175*, *176*, *190*). The chromium compounds usually undergo complete loss of carbon monoxide, the exceptions being $[Cr(CO)_5I]^-$ and (v-triars)Cr$(CO)_3$, which give $Cr(CO)_5I$ (*164*) and $[(\text{v-triars})Cr(CO)_2I]^+$ (*212*), respectively.

TABLE IX

OXIDATION PRODUCTS OF SUBSTITUTED TUNGSTEN CARBONYLS[a]

Starting material	Product		Ref.
$[W(CO)_5X]^-$		$[W(CO)_4X_3]^-$	(*164*)
diarsW$(CO)_4$	[diarsW$(CO)_4$I]I	diarsW$(CO)_3Br_2$	(*175*)
bipyW$(CO)_4$		bipyW$(CO)_3X_2$[b]	(*272*)
diphosW$(CO)_4$[c]		diphosW$(CO)_3I_2$	(*176*)
dithiaW$(CO)_4$		dithiaW$(CO)_3X_2$	(*189*)
ttasW$(CO)_3$	[ttasW$(CO)_3$X]X		(*66*)
tasW$(CO)_3$	[tasW$(CO)_3$X]X		(*190*)
v-triarsW$(CO)_3$	[v-triarsW$(CO)_3$X]X	v-triarsW$(CO)_2X_2$	(*212*)
hmbW$(CO)_3$	[hmbW$(CO)_3$X]X		(*266*)
diars$_2$W$(CO)_2$	[diars$_2$W$(CO)_2$X]X		(*175*)

[a] diars = o-$C_6H_4(AsMe_2)_2$, bipy = bipyridyl, diphos = $Ph_2PC_2H_4PPh_2$, dithia = 2,5-dithiahexane, ttas = PhAs(o-$C_6H_4AsPh_2)_2$, tas = $MeAs(CH_2CH_2CH_2AsMe_2)_2$, v-triars = $MeC(CH_2AsMe_2)_3$, hmb = hexamethylbenzene, and X = Cl, Br, I.

[b] X may also be HgCl (*111*).

[c] Evidence was obtained for the product [diphosW$(CO)_4$I]I_3, but the complex could not be isolated (*176*).

The ion $[W(CO)_4I_3]^-$ (*163*) and its tungsten(0) precursors $[W(CO)_5X]^-$ (X = halogen) (*2*, *95*, *198*) are the only known carbonyl halides of tungsten. When $[W(CO)_5X]^-$ is treated with an allyl halide, C_3H_5Y, a halogen-bridged, dimeric anion is obtained, $[(\pi\text{-}C_3H_5)W(CO)_2Y_3(CO)_2W(\pi\text{-}C_3H_5)]^-$. The bridge may be cleaved by pyridine to give $(\pi\text{-}C_3H_5)W(CO)_2Y\cdot py$ (*202*). Tungsten hexacarbonyl apparently does not react with allyl halides (*98*).

E. TUNGSTEN(III)

Further oxidation of (diars)W$(CO)_3Br_2$ gives [(diars)W$(CO)_3Br_2$]Br, in which the tungsten atom is still seven-coordinate but has a single unpaired electron, μ_{eff} = 1.54 B.M. (*175*).

F. TUNGSTEN(IV AND V)

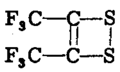
No carbonyl complex is known in which tungsten has an oxidation state higher than +3. The only aromatic group reported as coordinating to tungsten(IV) or tungsten(V) is cyclopentadienyl. Tungsten(IV) gives derivatives of the type $(\pi\text{-Cp})_2WX_2$, where X is H (*92, 123*) or halogen (*67*). In these compounds the two π-bonded rings are not parallel, the four groups forming a rough tetrahedron about the metal atom (*29, 100, 123*). The two π-bonded ligands are separated by a lone pair, which can be donated to a suitable acceptor, as in $[(\pi\text{-Cp})_2WH_3]^+$ and $(\pi\text{-Cp})_2WH_2.BF_3$ (*123, 126, 263*). The halogen compounds may be oxidized to the tungsten(V) derivative $[(\pi\text{-Cp})_2WX_2]X$ (X = Cl, Br) (*67, 71*).

VII. Other Compounds

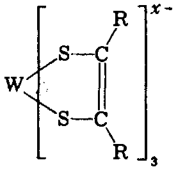
A few compounds do not fall readily into the above categories.

A. DITHIOLATES

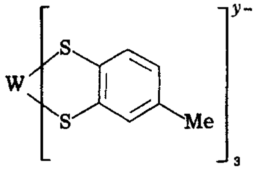
The reaction of bis(trifluoromethyl)-1,2-dithietene (XI) with tungsten hexacarbonyl gives a monomeric, diamagnetic complex $W(S_2C_2(CF_3)_2)_3$ (XII, R = CF_3, $x = 0$) (*74, 162*). Similar derivatives of diphenyldithietene and toluenedithiol have been obtained [XII, R = Ph, $x = 0$ (*282*); XIII, $y = 0$ (*269*)]. These are formally complexes of tungsten(VI).



(XI)



(XII)



(XIII)

Anionic species may be obtained by reduction [XII, R = CF_3, $x = 1$ (*74*); R = Ph, $x = 1, 2$ (*269*); XIII, $y = 1$ (*282*)]. The mononegative anions are paramagnetic, with a magnetic moment of 1.77 B.M. (XII, R = CF_3, $x = 1$), while the dinegative anions are diamagnetic. The esr spectra of the paramagnetic species give g values very close to 2.00 and show little or no anisotropy (*269*). This cannot be explained in terms of a distorted octahedral ligand field (*74*), and it is probable that the configuration is that of a trigonal prism. This configuration has been found for $Re(S_2C_2Ph_2)_3$ (*80*), with which the corresponding tungsten compound is isomorphous (*269*).

B. OXALATES

When a tungstate solution is reduced in the presence of oxalic acid, a red solution is obtained containing tungsten(V), from which salts of the anion $[WO_2(C_2O_4)_2]^{3-}$ may be obtained (*59*). These salts have been little studied but are useful intermediates, as in the preparation of oxyhalide complexes (*59*) or octacyanotungstates (*20*). This seems to be the only isolated oxalato complex of tungsten, in contrast to the many derivatives known for molybdenum.

C. PHENYL DERIVATIVES

Reduction of tungsten hexachloride or pentabromide with phenyllithium gives a black, diamagnetic, air-sensitive solid which has been formulated both as $Ph_3W{\cdot}3LiPh{\cdot}3Et_2O$ (*104*) and as $Ph_4W{\cdot}2LiPh{\cdot}3Et_2O$ (*246*). This product may be hydrogenated, when 2 moles of hydrogen are taken up, and another reactive solid has been isolated which was formulated as $WH{\cdot}2LiPh$ (*247*).

VIII. Metal-Metal Bonds

Compounds in which there are metal-metal bonds occur under two sets of circumstances:

(a) A wide variety of transition metals form metal-metal bonds when the metal is in a low oxidation state and the ligands are strongly π-bonding (*57*). The metal-metal bonding in these systems is a function more of the ligands than of the metal, since the ligands can, by delocalization of the metal electrons, make the metal more electronegative and reduce the repulsion between nonbonding electrons.

(b) Metals with high heats of atomization are prone to the formation of cluster compounds and their other compounds often exhibit metal-metal bonds (*248*). These properties presumably result from the occurrence of the optimum number of *d* electrons and available orbitals and of good overlap between these orbitals. Tungsten has the highest heat of atomization of all the transition metals (Table X).

Tungsten shows examples of both types of compound (Table XI). Many of the low oxidation state compounds are stabilized by metal-metal bonds, and the compounds are diamagnetic. The metal-metal bonds are not very strong unless reinforced by bridging ligands. Crystallographic data are available only for the cyclopentadienyltricarbonyl, $[\pi\text{-CpW(CO)}_3]_2$, in which the two halves of the molecule are united only by a tungsten-tungsten bond of length 3.28 Å (cf. 2.74 Å in the metal) (*290*). This bond is readily cleaved, either by oxidation, e.g. with halogens to give $\pi\text{-CpW(CO)}_3X$, or by reduction, e.g. with sodium to give $[\pi\text{-CpW(CO)}_3]^-$.

Despite the formal changes in oxidation state, the total number of electrons associated with the tungsten atom is the same in all these compounds, all are "eighteen-electron" compounds. A similar tungsten-tungsten bond presumably occurs in $[W_2(CO)_{10}]^-$.

Crystallographic data are available also for the dioxide, WO_2 (*130*), and for the enneachloride, $[W_2Cl_9]^{3-}$ (*41*, *283*). In both these compounds the metal-metal bonds are shorter than in the metal (metal, 2.74 Å; WO_2, 2.49 Å; $K_3W_2Cl_9$, 2.41 Å) and are probably multiple bonds. The chloro complex provides a good example of the ease with which the heavier metals form metal-metal bonds compared to the lighter metals. The chromium complex, $Cs_3Cr_2Cl_9$, is paramagnetic, μ_{eff} = 3.82 B.M. per chromium atom. The anion is symmetrical (D_{3h}) and the two chromium atoms repel each other to a distance of 3.12 Å (cf. 2.45 Å in chromium metal) (*286*). The corresponding titanium and vanadium complexes are isomorphous with the chromium compound (*286*). The molybdenum and tungsten derivatives are diamagnetic, however, and the structure of $K_3W_2Cl_9$ shows that the tungsten atoms are drawn together. The anion is slightly distorted by twisting of the triangle of bridging chlorine atoms about the trigonal axis. It would be of interest to determine whether this distortion occurs in salts with other cations.

TABLE X

HEATS OF ATOMIZATION OF TRANSITION METALS

(kcal/g-atom) (*248*)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
80	113	123	95	69	100	102	102	81
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
102	146	175	158	155	155	133	84	68
La	Hf	Ta	W	Re	Os	Ir	Pt	Au
100	168	187	202	186	162	160	135	87

TABLE XI

COMPOUNDS IN WHICH METAL-METAL BONDING PROBABLY OCCURS

$[\pi\text{-Cp}(CO)_3W]_2$
$[(CO)_5W]_2^-$
$[W_2(CO)_9]^{4-}$
$[W_3(CO)_{14}]^-$
$[(CO)_4(LR_2)W]_2$

W_6X_{12}, W_6X_{14}, W_6X_{16}, W_6X_{18}
WX_4
WX_5
$[W_2X_9]^{3-}$
$W_2X_6L_3$
WO_2
$W_2(OEt)_6Cl_4$

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