Discussion

The rare earth disilicides crystallize in the $ThSi_2$-, $GdSi_2$-, and AlB_2-type structures at the ideal AB_2 stoichiometry or close to it. Compounds crystallizing in these structures at nonstoichiometric compositions are found to contain vacancies in the B atom positions.

Substitution of Al for Si extends the AlB_2- and the $ThSi_2$-type disilicides into the ternary system. The $GdSi_2$-type structure is stable only in the binary alloys. It is known that the $GdSi_2$-type structure is derived from the $ThSi_2$-type structure by slight structural distortions. Also continuous transformation from the $ThSi_2$-type to the $GdSi_2$-type has been found in the La–Si system.[10] Our results indicate that the orthorhombic distortion is not retained in ternary alloys and the $ThSi_2$-type structure extends deep into the ternary systems. A similar result has been obtained in the Ti–Al–Si system for the $ZrSi_2$-type ternary phase.[11]

The AlB_2-type structure does not occur in the lanthanum and cerium disilicides. It is not found in the digermanides of the light rare earths starting from La to Gd. No rare earth distannide is known to possess the AlB_2-type structure. Our results show that the AlB_2-type structure is stabilized in several ternary compounds of the rare earths on the $(RE)Al_2$–$(RE)Si_2$, –$(RE)Ge_2$, and –$(RE)Sn_2$ sections. Substitutions of large amounts of Al for Si or Ge in the $ThSi_2$-type phases leads to a change in the structure to the AlB_2-type.

It is generally believed that Al, since it has only three valence electrons, reduces the over-all valence electron concentration when it is added to the rare earth disilicides or digermanides. This assumption can be valid and applicable especially for those alloys which are rich in nontransition metal atoms. On this basis we hypothesize that a reduction in the valence electron concentration of the $ThSi_2$-type compounds leads to the stabilization of the AlB_2-type structure.

Substitution of Si, Ge, or Sn for Al atoms in the $(RE)Al_2$ compounds stabilizes the AlB_2-type structure. In the binary and ternary alloys of group IV and V transition elements with similar nontransition elements the $MgZn_2$-type occurs. Hence, it can be concluded that the $MgZn_2$-type occurs at higher valence electron concentrations than those for the $MgCu_2$-type. However, an increase in the valence electron concentration through substitution of Si, Ge, or Sn for Al in the $(RE)Al_2$ compounds does not stabilize the $MgZn_2$-type structure.

Alloys on the $GdAl_2$–$GdSi_2$ section indicate that the defects in the AlB_2-type binary silicide Gd_3Si_5 are not removed on alloying with Al. No AlB_2-type phase is found on the $GdAl_2$–$GdGe_2$ and $GdAl_2$–$GdSn_2$ sections. In the former section the $MgCu_2$-type phase, $GdAl_2$, is found to be in equilibrium with the $ThSi_2$-type phase, $GdGe_2$.

The occurrence of the Laves phases in transition metal alloys that have valence electron concentrations close to those of the transition metal disilicides is now better understood.[12] The partial structural sequence with respect to increasing valence electron concentration is obtained

$$MgCu_2 \longrightarrow (MgZn_2) \longrightarrow AlB_2 \longrightarrow ThSi_2 \longrightarrow GdSi_2$$

The AlB_2-type ternary phases possess maximum volumes per atom; this quantity decreases as the structure changes from the AlB_2 type on either side of the structural sequence. This anomaly cannot be explained on the basis of normal atomic volumes of Al or Si atoms, deduced from the pure elemental structures. More work needs to be done in order to account for this anomalous increase in volume in the AlB_2-type ternary phases.

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Coordination Chemistry of Tungsten Dioxodichloride

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A series of complex compounds of tungsten(VI) dioxodichloride of the types $WO_2Cl_2 \cdot 2L$ and $WO_2Cl_2 \cdot B$, where L = dimethylformamide, triphenylphosphine oxide, hexamethylphosphoramide, dimethyl sulfoxide, tetramethylene sulfoxide, or methyl cyanide and B = bipyridyl or phenanthroline, have been prepared by one or more of three preparative methods. The infrared and ultraviolet spectra of these compounds have been recorded and the results are discussed. The properties of two tungsten(V) oxotrichloride complexes formed under slightly different reaction conditions have also been examined.

Introduction

The coordination chemistry of molybdenum dioxodihalides has been examined extensively. Thus neutral complexes of the general formulas $MoO_2X_2 \cdot 2L$ (L = monodentate) and $MoO_2X_2 \cdot B$ (B = bidentate, X = Cl or Br) have been prepared by the reaction of MoO_2X_2 with ligands, with or without a solvent,[1-4] by halogen

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oxidation of substituted molybdenum carbonyls,[5,6] and by the reaction of molybdenum pentachloride with oxygen ligands.[7] In a few instances 1:1 complexes have been isolated with monodentate ligands. For example MoO_2Cl_2 yields 1:1 or 1:2 adducts with some alkyl cyanides under different reaction conditions.[4]

The corresponding tungsten compounds are however very poorly characterized, presumably because the insolubility of tungsten dioxodihalides in common organic solvents makes their preparation more difficult than that of their molybdenum analogs. Consequently the few known adducts of WO_2X_2 have usually been prepared by the oxidation of substituted carbonyl derivatives, and only in one report have such compounds been prepared by the direct interaction of tungsten dioxodichloride with oxygen ligands.[8]

This paper describes the preparation and properties of several tungsten dioxodichloride complexes obtained by one or more of three methods.

Experimental Section

Analysis.—Halogen and oxidation state determinations were carried out as previously described.[9] Tungsten was usually determined as the trioxide by strong ignition of a sample of the complex moistened with concentrated nitric acid. This procedure was unsatisfactory in the presence of phosphorus; consequently, such compounds were hydrolyzed with aqueous alkali containing a little hydrogen peroxide, and tungstic acid precipitated from the filtrate as the cinchonine complex. This was finally ignited at red heat and weighed as tungsten trioxide. Carbon, hydrogen, and nitrogen were determined by a professional analyst.

Spectral and Magnetic Measurements.—The visible spectra of solids and solutions were measured on a Unicam SP500 spectrophotometer. Measurements in the ultraviolet region were recorded in methyl cyanide or methylene dichloride solutions on a Perkin-Elmer 137 spectrophotometer. Infrared spectra were examined as Nujol mulls between NaCl plates with a Perkin-Elmer 237 spectrophotometer. Magnetic susceptibilities were measured at room temperature (295°K) on a Gouy balance. The magnetic moments reported below have been corrected for diamagnetism.

Conductivity Measurements.—Determinations were made on a Wayne-Kerr Autobalance Universal Bridge at 20 ± 1°.

Materials.—The purest grade commercially available chemicals were used without further purification except where specified.

Acetone and ether used as solvents in many of the preparations were dried over calcium chloride. Methyl cyanide and methylene dichloride were dried more rigorously by distillation from phosphorus pentoxide. The liquid ligands used were purified by given literature procedures,[10,11] and solid ligands were pumped and heated *in vacuo* to remove traces of moisture.

Tungsten dioxodichloride was prepared by subliming tungsten hexachloride in a stream of dry oxygen gas. The small amount of tungsten oxotetrachloride formed was sublimed away. *Anal.* Calcd for WO_2Cl_2: W, 64.1; Cl, 24.7. Found: W, 63.8; Cl, 24.8; μ, 0.20 BM; oxidation state, 6.00.

Preparation of Complexes.—The complexes were prepared by one or more of three methods, although procedural details differed slightly for each product. The complexes were all prepared several times so that the analyses given are the mean of results on several preparations.

Method A.—Several complexes were prepared by the direct reaction of tungsten dioxodichloride with excess pure ligand maintained above its melting point for at least 12 hr in an inert atmosphere.

$WO_2Cl_2 \cdot C_8H_6N_2$.—An excess of dipyridyl (1.50 g) was heated to ~30° above its melting point in an atmosphere of nitrogen while small quantities of tungsten dioxodichloride were added until the reaction mixture contained 0.20 g of WO_2Cl_2. After 12 hr at 100° the melt was cooled and the solid was crushed and washed with ethanol and ether. The product was isolated in 65% yield (0.20 g). *Anal.* Calcd for $WO_2Cl_2 \cdot C_8H_6N_2$: W, 41.5; Cl, 16.0; C, 27.1; H, 1.82; N, 6.32. Found: W, 42.1; Cl, 16.1; C, 27.8; H, 1.67; N, 6.37; μ, 0.30 BM; oxidation state, 6.00.

$WO_2Cl_2 \cdot C_{12}H_8N_2$.—A similar procedure carried out at 130° and using the same weights of reactants as in the previous preparation yielded 0.25 g (77%) of a white solid. *Anal.* Calcd for $WO_2Cl_2 \cdot C_{12}H_8N_2$: W, 39.4; Cl, 15.2; C, 30.8; H, 1.73; N, 6.00. Found: W, 39.5; Cl, 15.0; C, 30.2; H, 1.80; N, 5.89; μ, 0.35 BM; oxidation state, 6.00.

Neither of these compounds melted below 320°.

$WO_2Cl_2 \cdot 2OP(C_6H_5)_3$.—This compound was prepared at 180° as above and purified by recrystallization from methylene dichloride–acetone. The product was obtained as white crystals in 27% yield, mp 274–276°. *Anal.* Calcd for $WO_2Cl_2 \cdot 2OP(C_6H_5)_3$: W, 21.8; Cl, 8.41; C, 51.2; H, 3.59. Found: W, 21.6; Cl, 8.48; C, 51.5; H, 3.65. The compound was diamagnetic.

All three of the above compounds are stable toward atmospheric moisture in the solid state and are slightly soluble in methylene dichloride, chloroform, and methyl cyanide, but insoluble in hydrocarbon solvents, ethers, acetone, or ethanol.

$WO_2Cl_2 \cdot 2CH_3CN$.—Anhydrous methyl cyanide (15 ml) reacted within 1 day with 0.30 g of WO_2Cl_2 in an evacuated sealed tube heated to 90°. Removal of excess nitrile at the pump left a white powder. *Anal.* Calcd for $WO_2Cl_2 \cdot 2CH_3CN$: W, 49.9; Cl, 19.2; C, 13.0; H, 1.64. Found: W, 50.2; Cl, 19.0; C, 12.6; H, 1.53.

The yield was quantitative. On heating the complex, slow decomposition occurred over a long temperature range (100–150°). The same product was formed by the reaction of WO_2Cl_2 with methyl cyanide at room temperature. A reaction time of at least 10 days was necessary to dissolve the WO_2Cl_2 and the product was formed as large colorless crystals. Reaction in sealed tubes at temperatures above 100° resulted in some reduction of the hexavalent tungsten as indicated by the formation of a deep green, slightly paramagnetic solution.

Method B.—An acetone solution of tungsten hexachloride was added to excess ligand dissolved in acetone. Several complexes precipitated on standing at 0°; others required the addition of ether to initiate precipitation.

$WO_2Cl_2 \cdot 2C_2H_6OS$.—Tungsten hexachloride (0.50 g) was dissolved in 10 ml of acetone and added to 1 ml of dimethyl sulfoxide (DMSO) in 5 ml of acetone. The green solution turned brown and deposited white crystals on standing at 0°. The product was washed with acetone and ether; yield, 0.43 g, 77%; mp 78° dec. *Anal.* Calcd for $WO_2Cl_2 \cdot 2C_2H_6OS$: W, 41.5; Cl, 16.0; C, 10.8; H, 2.73. Found: W, 41.2; Cl, 16.0; C, 11.2; H, 2.62.

$WO_2Cl_2 \cdot 2C_4H_8OS$.—This compound was prepared in 68% yield from tetramethylene sulfoxide (TMSO) and tungsten hexachloride in exactly the same way as $WO_2Cl_2 \cdot 2DMSO$; mp 117–119° dec. *Anal.* Calcd for $WO_2Cl_2 \cdot 2C_4H_8OS$: W, 37.1; Cl, 15.0; C, 19.4; H, 4.10. Found: W, 37.0; Cl, 15.1; C, 19.0; H, 4.08.

Both sulfoxide complexes were diamagnetic and sparingly soluble in methyl cyanide but insoluble in all of the solvents mentioned above.

$WO_2Cl_2 \cdot 2OP(C_6H_5)_3$ and $WOCl_3 \cdot 2OP(C_6H_5)_3$.—The reaction of fresh acetone solutions of tungsten hexachloride with triphenyl-

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TABLE I

INFRARED SPECTRA OF WO_2Cl_2 AND $WOCl_3$ ADDUCTS (cm^{-1})

Compound	W–O absorption frequencies	M–O absorption frequencies (M = C, P, or S)	Other absorptions
WO_2Cl_2	845 sh, 810 s, 765 s, 740 sh		
$WO_2Cl_2 \cdot 2DMF$	913 s, 960 s, 965 s	1640 s, 1655 br	690 s N—C=O bend
$WO_2Cl_2 \cdot 2CH_3CN$	922 s, 972 s		2295 s C≡N str
$WO_2Cl_2 \cdot 2OP(C_6H_5)_3$	915 s, 960 s	1165 s, 1172 s	
$WOCl_3 \cdot 2OP(C_6H_5)_3$	973 s	1160 s, 1170 s	
$WO_2Cl_2 \cdot 2HMPA$	913 s, 954 s	1196 s	990 br, 750 s,
$WOCl_3 \cdot 2HMPA$	970 s	1196 s	990 br, 750 s P—N str
$WO_2Cl_2 \cdot dipy$	915 s, 953 s		
$WO_2Cl_2 \cdot phen$	915 s, 943 s		
$WO_2Cl_2 \cdot 2DMSO^a$	895 s, 910 s, 920 s, 945 s, 955 s, 986 s, 998 s, 1032 s		718 m, 725 m C—S str
$WO_2Cl_2 \cdot 2TMSO^a$	898 br, 912 sh, 930 s, 950 s, 978 m, 985 sh, 1005 w		725 m C—S str

[a] The bands in these complexes in the 900–1000-cm^{-1} region cannot be individually assigned to mainly W–O or S–O vibrations.

phosphine oxide produced green crystals which were a mixture of the title compounds. An excess of WCl_6 favored the formation of the tungsten(V) derivative, but it was never obtained completely free from the dioxodichloride complex, as indicated by analytical, magnetic, and infrared measurements. Typical figures gave W:Cl = 1:2.7; μ, 1.0 BM; oxidation state, 5.3. No attempts were made to optimize the yield of tungsten(V) compound by using different or mixed solvents. Pure $WO_2Cl_2 \cdot 2OP(C_6H_5)_3$ was prepared by dissolving 1.00 g of WCl_6 in 10 ml of acetone and oxidizing this solution with air or a dilute acetone solution of "100 volume" aqueous hydrogen peroxide until the deep green coloration was just discharged. This solution was then added to a solution of 1.00 g of triphenylphosphine oxide in 10 ml of acetone and on standing white crystals separated out. These were washed with acetone and ether and air dried; yield, 1.10 g, 52%. Analysis, infrared, and melting point determinations were identical with those of $WO_2Cl_2 \cdot 2OP(C_6H_5)_3$ prepared by method A.

$WO_2Cl_2 \cdot 2HMPA$ and $WOCl_3 \cdot 2HMPA$.—The reaction of 1.10 g of WCl_6 in 10 ml of acetone with 2 ml of hexamethylphosphoramide (HMPA) in 5 ml of acetone gave a brown solution, which on addition of 75 ml of ether and standing at 0° produced 1.37 g of large green and colorless crystals. The crystals were filtered off and washed with acetone and ether. The colorless crystals were easily handpicked and were found to be $WO_2Cl_2 \cdot 2C_6H_{18}N_3OP$. *Anal.* Calcd for $WO_2Cl_2 \cdot 2C_6H_{18}N_3OP$: W, 28.4; Cl, 11.0; C, 22.3; H, 5.61; N, 13.0. Found: W, 28.2; Cl, 11.1; C, 22.4; H, 5.93; N, 12.9, mp 210° dec. The green crystals were identified as $WOCl_3 \cdot 2HMPA$, usually contaminated with a little of the sexivalent complex. *Anal.* Calcd for $WOCl_3 \cdot 2C_6H_{18}N_3OP$: W, 27.6; Cl, 16.0; C, 21.6; H, 5.45; N, 12.6. Found: W, 27.7; Cl, 15.8; C, 21.9; H, 5.37; N, 12.6; mp 200–205 dec; μ, 1.40 BM.

The mixture of complexes produced by this method was soluble in dry chloroform or methylene dichloride, and in the presence of dry air or oxygen the turquoise solution became colorless. Addition of excess ether to this solution then precipitated pure $WO_2Cl_2 \cdot 2HMPA$. Both complexes were very hygroscopic unless completely freed from solvent and were quickly hydrolyzed in solution by traces of moisture.

$WO_2Cl_2 \cdot 2DMF$.—Addition of a fresh solution of WCl_6 in acetone to dimethylformamide (DMF) in acetone gave a brown solution. Ether was added until the solution became cloudy, and on standing at 0° a pale green solid precipitated out. This was washed with dry ether and pumped *in vacuo*. Analysis showed that the product was a mixture of tungsten(V) and -(VI) complexes. Typical figures were W:Cl = 1:2.3; μ, 0.4 BM. Pure $WO_2Cl_2 \cdot 2DMF$ was isolated in 80% yield from a solution of WCl_6 in acetone which had been oxidized with air or hydrogen peroxide before mixing with dimethylformamide. The product was washed with ether and decomposed only slowly under atmospheric conditions although the mixture of quinque- and sexivalent complexes was very susceptible to moisture. *Anal.* Calcd for $WO_2Cl_2 \cdot 2C_3H_7NO$: W, 42.5; Cl, 16.4; C, 16.6; H, 3.26; N, 6.47. Found: W, 42.1; Cl, 16.6; C, 16.8; H, 3.53; N, 6.58; mp 177° dec; diamagnetic. The compound was slightly soluble in CH_3CN but insoluble in the other solvents tried.

Method C.—Two complexes were prepared by ligand-replacement reactions. $WO_2Cl_2 \cdot 2L$ (L = CH_3CN or $OP(C_6H_5)_3$) were dissolved in dry methyl cyanide or methylene dichloride and a solution of the ligand in the same solvent was added. The precipitated complex was filtered off, washed with a little dry methylene dichloride, and pumped *in vacuo*. In this way $WO_2Cl_2 \cdot dipy$ and $WO_2Cl_2 \cdot phen$ were prepared in 90% yields.

Results and Discussion

Infrared measurements on the complexes are tabulated in Table I. Table II contains details of conductivity and ultraviolet measurements.

Infrared and other measurements on the dioxodihalides of molybdenum and tungsten have been interpreted in terms of an oxygen-bridged polymeric structure in the solid state and mainly monomeric molecules in the vapor phase.[12,13] It has been suggested that in chloroform solution the molybdenum dioxodihalides exist mainly as dimers, whereas tungsten dioxodihalides have been shown to be insoluble in most organic solvents.[12] We have confirmed the infrared results for solid WO_2Cl_2 in the 625–2000-cm^{-1} region which indicate a W–O–W polymeric structure.[12] This polymer is however slowly broken down in methyl cyanide at room temperature with the formation of $WO_2Cl_2 \cdot 2CH_3CN$. Unfortunately this compound is insufficiently soluble in suitable solvents for molecular weight studies to be carried out, but its properties are consistent with an octahedral monomer. Although this complex is easily hydrolyzed by moisture, it provides a useful starting material for the preparation of other

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TABLE II

CONDUCTIVITY MEASUREMENTS AND ULTRAVIOLET SPECTRA OF WO_2Cl_2 COMPLEXES

Compound	Molar conductivity in CH_3CN, ohm^{-1} cm^2	Concn $\times 10^{-3}$ *M*	Ultraviolet spectrum in CH_3CN or CH_2Cl_2, cm^{-1} [a]	Ligand absorptions
$WO_2Cl_2 \cdot 2CH_3CN$	8.4	0.70	34,300 (3.30)	...
			39,200 (3.47)	
			45,600 (3.68)	
$WO_2Cl_2 \cdot 2DMF$	6.0	0.66	36,800 sh (3.30)	...
			43,800 (3.78)	
$WO_2Cl_2 \cdot 2OP(C_6H_5)_3$	0.38	0.87	36,600 (3.79)	36,800 [b]
			37,400 (3.82)	37,600
			38,500 (3.77)	38,800
			43,400 (4.11)	44,400
$WO_2Cl_2 \cdot 2HMPA$	3.1	0.54	37,700 sh (3.30)	
			44,000 (3.70)	44,400
$WO_2Cl_2 \cdot 2DMSO$	0.51	0.80	38,800 sh (3.48)	...
			43,100 (3.78)	
$WO_2Cl_2 \cdot 2TMSO$	1.7	0.57	37,600 sh (3.40)	...
			43,000 (3.60)	
$WO_2Cl_2 \cdot dipy$	0.20	0.73	32,100 (4.05)	35,700 [c]
			39,800 (4.04)	42,600
			43,100 (4.11)	
$WO_2Cl_2 \cdot phen$	6.6	0.38	36,400 sh (4.11)	37,700 [c]
			36,900 (4.11)	
			43,500 (3.71)	43,950

[a] Extinction coefficients in parentheses expressed as log ϵ. [b] H. H. Jaffé, *J. Chem. Phys.*, **22**, 1430 (1954). [c] C. Favini and E. Paglia, *J. Inorg. Nucl. Chem.*, **8**, 155 (1958).

tungsten dioxodichloride adducts. All of the complexes, irrespective of their method of preparation, show W=O absorption bands in the 910–920- and 950–970-cm^{-1} regions indicating that they probably contain a discrete O=W=O group with *cis* rather than *trans* oxygen atoms. The complexes are nonelectrolytes in anhydrous methyl cyanide as indicated by their low molar conductivities listed in Table II. Those ligands with two potential donor atoms, such as DMF, bond *via* oxygen in these complexes as shown by the shift of the M—O stretching frequencies to lower wavenumbers (10–35 cm^{-1}) on coordination. Absorption bands associated with other parts of these ligand molecules usually show a slight increase in frequency on coordination through oxygen.[14–16] Thus the P—N stretching frequencies occur at 990 and 750 cm^{-1} in $WO_2Cl_2 \cdot 2HMPA$ compared with 980 and 740 cm^{-1} in the free ligand. Similarly the N—C=O bending frequency in DMF is increased from 657[14] to 690 cm^{-1} in the complex and the C—S stretching frequencies of 725 and 718 cm^{-1} in $WO_2Cl_2 \cdot 2DMSO$ are 28 and 21 cm^{-1} higher than that of the free ligand.[16] In the methyl cyanide complex $WO_2Cl_2 \cdot 2CH_3CN$, the C—N stretching frequency shows the usual increase upon coordination as noted for many nitrile adducts.[17] The combination band which occurs at 2293 cm^{-1} in free CH_3CN is shifted to 2325 cm^{-1} in the complex. The spectra of $WO_2Cl_2 \cdot 2DMSO$ and $WO_2Cl_2 \cdot 2TMSO$ between 900 and 1050 cm^{-1} are very complex so that no assignment can be attempted; however, the absence of bands in the 1050–1200-cm^{-1} region confirms that the attachment of the sulfoxides is through oxygen and not sulfur.[18]

The two tungsten(V) compounds show a single W–O stretching frequency near 970 cm^{-1} in agreement with other known tungsten(V) oxo species.[19,20]

Tungsten Hexachloride–Acetone Solutions.—The addition of WCl_6 to acetone gives initially a yellow solution which soon darkens, evolves hydrogen chloride, and turns deep green. This solution contains one or more tungsten(V) oxo species as shown by bands at 11,500 br, 14,800, 17,200 sh, and 26,000 sh cm^{-1} in the visible region. The $WOCl_5^{2-}$ ion absorbs at 12,800, 14,700 sh, and 26,000 cm^{-1}; the $WOCl_4^-$ ion has bands at 10,600, 18,500, and 25,000 cm^{-1};[21] and $WOCl_3 2L$ compounds (where L = $OP(C_6H_5)_3$ or HMPA) have visible spectra very similar to the $WOCl_5^{2-}$ ion (Table III). Attempts to isolate pure tungsten(V)–acetone complexes from these solutions were unsuccessful, but the addition of oxygen ligands, inert to hydrogen chloride, to a fresh solution of WCl_6 in acetone often produces $WOCl_3 \cdot 2L$ as well as $WO_2Cl_2 \cdot 2L$ complexes. On standing for several hours or on the addition of a few drops of hydrogen peroxide, the deep green coloration of acetone solutions of WCl_6 fades and the bands at 11,500, 14,800, and 17,200 cm^{-1} disappear. Addition of ligand now produces WO_2Cl_2 complexes only.

TABLE III

REFLECTANCE SPECTRA OF $WOCl_3$ ADDUCTS

Compound	Absorption max, cm^{-1}
$WOCl_3 \cdot 2OP(C_6H_5)_3$	13,100, 14,300 sh, 24,400
$WOCl_3 \cdot 2HMPA$	13,300, 14,800, 25,600
$WOCl_3$	13,100, 24,400 [a]

[a] G. W. A. Fowles and J. L. Frost, *Chem. Commun.*, 252 (1966).

In the case of DMSO and TMSO, only $WO_2Cl_2 \cdot 2L$ can be isolated from WCl_6 in acetone under any conditions. Any tungsten(V) present in solution is evidently oxidized by the sulfoxide with the formation of the corresponding sulfide which is easily detected in the filtrate by its smell. Thus the quinquevalent compound $WOCl_3 \cdot 2DMSO$ cannot be isolated under these conditions, as can the corresponding molybdenum complex. This exemplifies the lesser stability of tungsten(V) compared with molybdenum(V) oxo species as has been noted before.[6]

Spectral and Magnetic Measurements.—Most of the tungsten dioxodichloride adducts are diamagnetic, although $WO_2Cl_2 \cdot dipy$, $WO_2Cl_2 \cdot phen$, and WO_2CL_2 itself have small moments, presumably owing to temperature-independent paramagnetism. Similar values have been previously noted for octahedral Mo(VI) and W(VI) complexes.[6,22] The magnetic moment of

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$WOCl_3 \cdot 2HMPA$ which was the only pure quinquevalent tungsten compound isolated was found to be 1.40 BM. This value is a little lower than the room-temperature values of most $WOCl_5^{2-}$ and $WOCl_4^-$ salts,[19] but similar to the value reported for $WOCl_3 \cdot$dipy.[6]

The reflectance spectra of $WOCl_3 \cdot 2L$ (L = $OP(C_6H_5)_3$ and HMPA) given in Table III are very similar to that of the $WOCl_5^{2-}$ ion.[21]

No attempts will be made at present to assign the bands in view of the problems associated with heavy-metal d^1 oxo species.[19,23]

As expected the WO_2Cl_2 complexes do not absorb in the visible region; however, their ultraviolet spectra (Table II) show certain similarities when allowance is made for ligand absorptions. $WO_2Cl_2 \cdot 2CH_3CN$, $WO_2Cl_2 \cdot 2DMF$, $WO_2Cl_2 \cdot 2DMSO$, and $WO_2Cl_2 \cdot 2TMSO$ are the only compounds which should not exhibit internal ligand absorption bands, so the spectra of these complexes should show bands typical of the WO_2Cl_2 group. The first low-energy transition at 34.3 kK in $WO_2Cl_2 \cdot 2CH_3CN$ is fairly weak in intensity, and since this compound is very easily hydrolyzed it is possible that this band is caused by impurity or a ligand ↔ metal transition peculiar to CH_3CN since none of the other complexes exhibits a band in this region which is not attributable to the ligand. The other two bands at 39.2 and 45.6 kK are observed, usually at slightly lower wavelengths, in all of the complexes, with the exception of the triphenylphosphine oxide, dipyridyl, and phenanthroline compounds where ligand absorptions obscure these regions. Neumann and Cook[24] observed two bands in the ultraviolet spectra of Mo(IV) solutions which were characteristic of oxo species with a Mo:Cl ratio of 1:2, and these bands occurred at similar wavelengths to those of the WO_2Cl_2 ligand species.

The internal ligand transitions are generally observed at lower frequencies in the complexes than in the free ligand. This shift is quite large for dipyridyl as has been noted before.[25]

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The Reduction of Cobalt(III) by Neptunium(V) and the Neptunium(V)–Chromium(III) Complex[1]

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The rate law for the reaction Np(V) + Co(III) = Np(VI) + Co(II), from 5 to 25° in perchloric acid–lithium perchlorate solutions of constant ionic strength, is $-d[Np(V)]/dt = k'[Np(V)][Co(III)]$ where $k' = k_0 e^{-\beta[H^+]}$. Under the same conditions, the rate law for the reaction Co(III) + Np(V)·Cr(III) = Co(II) + Np(VI) + Cr(III) is $-d[Np(V)\cdot Cr(III)]/dt = k_c'[Np(V)\cdot Cr(III)][Co(III)]$ where $k_c' = k_c''[H^+]^{-1}e^{-\beta'[H^+]}$. Presumably the exponential factor in each of these rate laws is caused by mild medium effects.

Introduction

The oxidation of the hydrated Np(V) ion to Np(VI) involves minimal changes in the primary coordination spheres of these species. The question posed is what effect will a weak complex between Np(V) and Cr(III) have, in terms of the relevant kinetic parameters, when a common reagent Co(III) is used as the oxidant? This communication presents the results obtained in such a comparative kinetic study.

Experimental Section

Reagents.—The preparation and standardization of the Np(V), perchloric acid, and lithium perchlorate solutions have been described in a previous publication.[3] Fresh stock solutions of the Np(V)·Cr(III) complex were prepared prior to use by the ion-exchange procedure previously described for the isolation of the Np(V)·Rh(III) complex.[4]

Cobaltous perchlorate was prepared from reagent grade cobaltous carbonate and perchloric acid. The perchlorate salt was recrystallized twice from perchloric acid. The crystals were then dissolved in triple-distilled water. Cobalt(III) perchlorate solutions were prepared both by electrolytic oxidation of the cobaltous perchlorate and in a few cases from the cobalt(III) carbonate complex following the procedure outlined by Hofmann-Bang and Wulf.[5]

Procedures. A. The Np(V)–Co(III) Reaction.—The molar extinction coefficient of Co(III) at 6020 A was determined as $34.5 \pm 0.1\ M^{-1}\ cm^{-1}$ in 1 M perchloric acid.[6] The stoichiometry of the reaction

$$Co(III) + Np(V) = Co(II) + Np(VI) \qquad (1)$$

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[1] Based on research performed under the auspices of the U. S. Atomic Energy Commission.

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[6] This is in excellent agreement with the value of $34.76\ M^{-1}\ cm^{-1}$ determined by D. W. Weiser, Ph.D. Dissertation, University of Chicago, June 1956.