TABLE IX

M–N STRETCHING FREQUENCY AND ELECTRONIC STRUCTURE IN THE $[M(bipy)_3]^{n+}$ TYPE COMPOUNDS (cm^{-1})[a]

	–I	0	I	II	III
d^3				V 374 (3.67) 335 $(t_{2g})^3$	Cr 385 (3.78) 349 $(t_{2g})^3$
d^4		Ti 374 (0) 339 $(t_{2g})^4$-ls		Cr 351 (2.9) 343 $(t_{2g})^4$-ls	
d^5	Ti 365 (1.74) 322 $(t_{2g})^5$-ls	V 371 (1.68) 343 $(t_{2g})^5$-ls	Cr 371 (2.0) 343 $(t_{2g})^5$-ls	Mn 224 (5.95) 191 $(t_{2g})^3(e_g)^2$-hs	Fe 384 (?) 367
d^6		Cr 382 (0) 308 $(t_{2g})^6$		Fe 386 (0) 376 $(t_{2g})^6$	Co 378[b] (0) 370[b] $(t_{2g})^6$
d^7		Mn 258 (4.10) 227 $(t_{2g})^5(e_g)^2$		Co 266 (4.85) 228 $(t_{2g})^5(e_g)^2$	
d^8	Mn 235 (3.71) 184 $(t_{2g})^6(e_g)^2$		Co 244 (3.3) 194 $(t_{2g})^6(e_g)^2$	Ni 282[c] (3.10) 258 $(t_{2g})^6(e_g)^2$	
d^9		Co 280 (2.23) 257 $(t_{2g})^6(e_g)^3$		Cu 291 (?) 268 $(t_{2g})^6(e_g)^3$	
d^{10}				Zn 230[c] (0) 184 $(t_{2g})^6(e_g)^4$	

[a] The numbers at upper right of each group indicate the M–N stretching frequencies (cm^{-1}). The number in parentheses gives the observed magnetic moment in units of Bohr magnetons.[4] ls = low spin; hs = high spin. [b] Values for $[Co(phen)_3](ClO_4)_3$. [c] Taken from ref 8.

between these two groups of investigators[33,34] concerning the interpretation of the electronic spectrum of $Ti(bipy)_3$. Our present infrared study suggests that the metal–bipy bonding is predominantly ionic in all these zerovalent complexes.

The degree of σ and π bonding of the M–N bond has been a subject of the nmr contact shift studies.[28,35,36] Again, some confusion exists concerning the interpretation of the observed nmr contact shifts. It is difficult, however, to deduce such information from vibrational spectra unless a rigorous normal-coordinate analysis is carried out by using a suitable potential field.

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Metal Complexes of Substituted Dithiophosphinic Acids. VI. Reactions of Difluorodithiophosphinic Acid with Chlorides and Oxychlorides of Chromium, Molybdenum, and Tungsten

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The reaction of difluorodithiophosphinic acid, F_2PS_2H, with O_2CrCl_2 gave the known $Cr(S_2PF_2)_3$ complex while $OMoCl_4$, $MoCl_5$, $MoCl_4$, $OWCl_4$, and WCl_6 gave new difluorodithiophosphinato complexes of the metals in reduced valence states. WCl_4, $WCl_4 \cdot 2py$, K_3MoCl_6, and molybdenum and tungsten metals did not react. The complex $K_3W_2Cl_9$ reacted to give a product which is thought to contain the $[W_2Cl_7S]^{3-}$ anion rather than the difluorodithiophosphinato complex. Aerial oxidation of the $Mo(S_2PF_2)_3$ afforded $OMo(S_2PF_2)_2$. Pyridine reacts with the $OMo(S_2PF_2)_2$ complex to form the complex $OMo(S_2PF_2)_2 \cdot 4py$ which does not contain coordinated dithiophosphinato ligands. The complexes $OMo(S_2PF_2)_2$ and $OW(S_2PF_2)_2Cl$ are the first reported oxodifluorothiophosphinato complexes of second- and third-row transition metals.

A series of transition metal salts of the strong acid F_2PS_2H[1] prepared by the reactions of the acid with the metal (Cr, Mn, Fe, Co, Ni, Cu), the metal oxide (Ag), or halide (Rh, Pd, Pt, $(C_6H_5)_3PAu$) have recently been reported.[2] The preparations of the V^{III} and OV^{IV} fluoro[3] and other[3-7] substituted dithiophosphinates have

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(1) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 281 (1969); R. W. Mitchell, M. Lustig, F. A. Hartman, J. K. Ruff, and J. A. Merritt, *J. Amer. Chem. Soc.*, **90**, 6329 (1968).

(2) F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, **9**, 629 (1970).

TABLE I

REACTIONS OF F_2PS_2H WITH CHLORIDES OR OXYCHLORIDES OF Cr, Mo, OR W[a]

Reagent	F_2PS_2H[b] consumed	HCl[b]	Product	Color	Subl temp,[c] °C	Mp,[d] °C	μ_{eff}[e]	By-products
O_2CrCl_2	~4.0	*f*	$Cr(S_2PF_2)_3$	Purple	100	52	3.87[4]	SPF_3, OPF_3, $P_2F_4O_3$
$OMoCl_4$	~2.4	~2.4	$OMo(S_2PF_2)_2$	Green	60	144–145	Dia	$(F_2PS_2)_2$
$MoCl_5$	~5.0	~5.0	$Mo(S_2PF_2)_3$	Red	20	62	3.53	$(F_2PS_2)_2$
$MoCl_4$	*f*	1.85						
$OWCl_4$	3–3.7	~3.5	$OWCl(S_2PF_2)_2$	Olive-brown	100			$(F_2PS_2)_2$, SPF_2Cl
WCl_6	~3.2	~3.0	$Cl_2W(S_2PF_2)_3$	Brown	120	>150		SPF_2Cl, WS_n
$K_3(W_2Cl_9)$	*f*	*f*	$K_3(W_2Cl_7S)$	Brown				SPF_2Cl

[a] No reaction with WCl_4, $WCl_4 \cdot 2py$, or $K_3(MoCl_6)$. [b] Molar ratio for a typical experiment. [c] At a pressure of 10^{-4} mm. [d] Sealed capillaries, uncorrected. [e] Bohr magnetons; Faraday method. [f] Mixture with by-products of the reaction, not estimated.

been described. A number of organometallic difluorodithiophosphinates of Mo,[8,9] W,[8,9] Cr,[9] Rh,[10] Fe,[8] and Mn[8] have been prepared. The strongly chelating nature of the $F_2PS_2^-$ ligand has been demonstrated as well as its ability to act as a monodentate or as a bridging ligand.[3-10]

We now report the reactions of a number of chlorides and oxide chlorides of Cr, Mo, and W with F_2PS_2H which extend the chemistry of these systems and in the case of Mo and W oxide chlorides provide new oxymetal difluorodithiophosphinate derivatives to compare with the vanadyl system.[3] The reactions are summarized in Table I.

Experimental Section

The reagents F_2PS_2H,[1] $OMoCl_4$,[11] $MoCl_5$,[12] $MoCl_4$,[13] $OWCl_4$,[12] WCl_4,[14] $WCl_4 \cdot 2py$,[14] $K_3[MoCl_6]$,[15] and $K_3[W_2Cl_9]$[16] were prepared according to published procedures. All reactions were performed in previously evacuated glass vessels, and all materials were handled using standard vacuum and inert-gas techniques. Analyses were performed by the analytical service of the Department of Chemistry, University of Alberta, or at the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Spectra were recorded on the following instruments: infrared (Perkin-Elmer PE 337), far-infrared (Beckman IR11), Raman (Carson's Laboratories 10SP Ar^+/Kr^+ laser, Spex 1401 monochromator, cooled FW 130 photomultiplier, and photon-counting electronics), mass spectra (AEI MS9 or MS12),^{19}F nmr (Varian A56-60 or HA100). Magnetic susceptibilities were obtained using the Faraday method, on a balance constructed in this laboratory.

For each reaction a typical, reproducible experiment is reported and a summary is given in Table I.

Reactions of Difluorodithiophosphinic Acid. (a) **With Chromyl Chloride.**—Chromyl chloride, O_2CrCl_2 (0.119 g, 0.767 mmol), and F_2PS_2H (0.515 g, 3.84 mmol) were mixed at −196° and allowed to warm slowly. At approximately −20° the reaction mixture reacted suddenly and vigorously to deposit a fine, gray, unidentified powder throughout the apparatus (which had a volume of approximately 1 l.) and to leave in the reaction vessel a purple solid. [*Caution!* Although this reaction is not exceptionally exothermic, it does proceed vigorously with the evolution of large quantities of gaseous reaction products, some of which are pyrophoric (*e.g.*, SPF_3). Attempts to perform this reaction on a larger scale should be accompanied by appropriate safety precautions.] Fractionation of the volatile reaction products gave mixtures containing, as major components, PF_3, OPF_3, OPF_2Cl, SPF_3, HO_2PF_2, and HCl, with some $F_4P_2O_3$, and excess F_2PS_2H, all identified by their infrared, mass, and ^{19}F nmr spectra. The purple solid was heated (100° (10^{-4} mm)) to yield, as a purple, crystalline sublimate, tris(difluorodithiophosphinato)chromium(III) (0.07 g, 21%), mp 52°, also identified by comparison of its infrared spectrum with that of an authentic sample.[4]

(b) **With Oxomolybdenum Tetrachloride.**—Oxomolybdenum tetrachloride, $OMoCl_4$ (0.181 g, 0.713 mmol), and F_2PS_2H (0.999 g, 7.450 mmol) were mixed at −196° and allowed to warm slowly to room temperature. Above −20° the mixture reacted smoothly to give a brown solution from which a green-brown mass was subsequently precipitated. After standing at room temperature for 18 hr the mixture was fractionated to give HCl (0.0598 g, 1.640 mmol), excess unreacted F_2PS_2H (0.387 g), and, after refractionation to remove dissolved F_2PS_2H, $(F_2PS_2)_2$ (0.1254 g, 0.472 mmol), and a green solid mass. Green diamagnetic needles were obtained by sublimation at 60° (10^{-4} mm) and were characterized as bis(difluorodithiophosphinato)oxomolybdenum(IV) (0.1788 g, 68%), mp 144–145° *Anal.* Calcd for $F_4MoOP_2S_4$: F, 20.08; Mo, 25.36; P, 16.37; S, 33.95; mol wt (CH_2Br_2 solution), 378; *m/e* (^{98}Mo, ^{32}S), 379.7299. Found: F, 21.66; Mo, 24.63; P, 16.05; S, 33.94; mol wt (CH_2Br_2 solution), 413; *m/e* (^{98}Mo, ^{32}S), 379.7296.

The green crystals readily dissolved in nonpolar organic solvents to form golden orange solutions, from which $OMo(S_2PF_2)_2$ was easily recovered by removal of the solvent under reduced pressure. In contrast, addition of cyclohexane to a saturated pyridine solution of $OMo(S_2PF_2)_2$ gave a dark green crystalline product which was identified as bis(difluorodithiophosphinato)oxotetrapyridinemolybdenum(IV) (>98%). *Anal.* Calcd for $C_{20}H_{20}F_4MoN_4P_2S_4$: C, 34.59; H, 2.91; N, 8.08; S, 18.47. Found: C, 33.57; H, 3.18; N, 8.05; S, 17.60. The ^{19}F nmr (pyridine solution) of this complex showed only a sharp, simple doublet (ϕ_F +1.9 ppm relative to $CFCl_3$ (J_{FP} = 1164 cps)) due to the free $F_2PS_2^-$ ion in pyridine.

In water $OMo(S_2PF_2)_2$ was sparingly soluble and readily hydrolyzed to the blue molybdenum oxide.

(c) **With Molybdenum Pentachloride.**—Molybdenum pentachloride (0.2285 g, 0.837 mmol) and F_2PS_2H (excess) were mixed at −196° and allowed to warm to room temperature. Above −20° the reagents slowly reacted to form a red solution. After being allowed to react at room temperature for 18 hr, the mixture was fractionated to give HCl (<0.167 g, 4.6 mmol) contaminated with a little SiF_4 and F_2PS_2H, excess F_2PS_2H, $(F_2PS_2)_2$ (0.187 g, 0.701 mmol), and a red, crystalline, volatile solid. The solid slowly sublimed (20° (10^{-4} mm)) onto a cooled probe (0°) to afford red, paramagnetic (μ_{eff} = 3.53 BM; see Table III), crystalline tris(difluorodithiophosphinato)molybdenum(III) (0.153 g, 36%), mp 62°. *Anal.* Calcd for $F_6MoP_3S_6$: F, 23.03; Mo, 19.36; P, 18.77; S, 38.88; *m/e* (^{98}Mo, ^{32}S), 496.6496. Found: F, 22.90; Mo, 18.99; P, 18.79; S, 38.29; *m/e* (^{98}Mo, ^{32}S), 496.6498.

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(3) R. G. Cavell, E. D. Day, W. Byers, and P. M. Watkins, *Inorg. Chem.*, **11**, 1591 (1972).

(4) R. G. Cavell, W. Byers, and E. D. Day, *ibid.*, **10**, 2710 (1971).

(5) R. G. Cavell, W. Byers, E. D. Day, and P. M. Watkins, *ibid.*, **10**, 2716 (1971).

(6) R. G. Cavell, W. Byers, E. D. Day, and P. M. Watkins, *ibid.*, **11**, 1598 (1972).

(7) R. G. Cavell, E. D. Day, W. Byers, and P. M. Watkins, *ibid.*, **11**, 1759 (1972).

(8) L. W. Houk and M. Lustig, *ibid.*, **9**, 2462 (1970).

(9) J. K. Ruff and M. Lustig, *ibid.*, **7**, 2171 (1968).

(10) F. A. Hartman and M. Lustig, *ibid.*, **7**, 2669 (1968).

(11) R. Colton, I. B. Tomkins, and P. W. Wilson, *Aust. J. Chem.*, **17**, 496 (1967).

(12) R. Colton and I. B. Tomkins, *ibid.*, **18**, 447 (1965).

(13) M. L. Larson and F. W. Moore, *Inorg. Chem.*, **3**, 285 (1964).

(14) R. E. McCarley and T. M. Brown, *ibid.*, **3**, 1232 (1964).

(15) L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Aust. J. Chem.*, **18**, 1569 (1965).

(16) R. A. Landice and R. C. Young, *Inorg. Syn.*, **6**, 153 (1960).

In organic solvents under vacuum, $Mo(S_2PF_2)_3$ readily dissolved to form red solutions from which the complex was easily recovered unchanged by removal of the solvent under reduced pressure. In water the crystals were sparingly soluble and readily hydrolyzed. In all of the above solutions oxidation of the Mo(III) complex was rapid upon exposure to air.

In air solid $Mo(S_2PF_2)_3$ slowly oxidized to the green $OMo(S_2PF_2)_2$, identified by comparison of its spectral properties with those of an authentic sample (above).

(d) **With Molybdenum Tetrachloride.**—Molybdenum tetrachloride (0.0422 g, 0.1775 mmol) and F_2PS_2H (0.781 g, 5.82 mmol) were mixed at −196° and warmed to room temperature. The $MoCl_4$ slowly dissolved and gently reacted to give initially a green solution which had turned to red after 12 hr of reaction. After 60 hr at room temperature the reaction mixture was separated, yielding HCl (0.012 g, 0.329 mmol), excess F_2PS_2H (0.652 g), and a dark red solid mass. Low yields of crystalline $Mo(S_2PF_2)_3$ were obtained by sublimation (50° (10^{-4} mm)), and the product was identified by comparison of its spectra with those of an authentic sample (above).

Repeating the experiment at 70° (1 day) gave similar results. However, at 70° (14 days) a brown-black solid was formed, from which no sublimable (120° (10^{-4} mm)) component was isolated.

(e) **With Potassium Hexachloromolybdate(III).**—Potassium hexachloromolybdate, $K_3[MoCl_6]$, did not react with excess F_2PS_2H at 25 or 70°, and starting materials were quantitatively recovered.

(f) **With Oxotungsten Tetrachloride.**—Oxotungsten tetrachloride, $OWCl_4$ (0.1298 g, 0.371 mmol), and F_2PS_2H (0.7303 g, 5.44 mmol) were mixed at −196° and allowed to warm to room temperature. On dissolution of $OWCl_4$ a yellow-brown solution which slowly deepened in color was formed. After 16 hr at room temperature a bulky precipitate was noted. Separation of the reaction mixture gave HCl (0.0548 g, 1.503 mmol) contaminated with traces of $F_2P(S)Cl$, SiF_4, and F_2PS_2H, excess F_2PS_2H, $(F_2PS_2)_2$[17] (0.434 g, 0.163 mmol), and an olive-brown residue. Heating (120° (10^{-4} mm)) the residue gave an olive-brown sublimate identified as chlorobis(difluorodithiophosphinato)oxotungsten(V) (0.034 g, 0.068 mmol, 18%), mp >150°. *Anal.* Calcd for $ClF_4OP_2S_4W$: Cl, 7.08. Found: Cl, 7.51. There remained a dark brown residue (Found: Cl, 4.04; S, 23.06) which contained a difluorodithiophosphinato complex (ir spectrum) which has not yet been identified.

Under reflux conditions for long periods of time, similar results with comparable or lower yields were obtained.

(g) **With Tungsten Hexachloride.**—Tungsten hexachloride (0.3830 g, 0.967 mmol) and F_2PS_2H (1.7275 g, 12.87 mmol) were mixed at −196° and subsequently warmed to room temperature. Above 0° WCl_6 dissolved and reaction occurred to give a dark brown solution from which a dark brown mass was precipitated. After 2.5 hr at room temperature the mixture was separated to give a mixture of HCl, SPF_3, SPF_2Cl, and SiF_4 (0.2346 g), excess F_2PS_2H (1.3092 g, consumed 0.4183 g, 3.12 mmol, 323%), and a dark brown mass. A brown microcrystalline sublimate was obtained upon heating (100–120° (10^{-4} mm)) which was identified as dichlorotris(difluorodithiophosphinato)tungsten(V), mp >150°. *Anal.* Calcd for $Cl_2F_6P_3S_6W$: Cl, 10.84; F, 17.44; S, 29.59; W, 28.14. Found: Cl, 11.05; F, 17.44; S, 29.92; W, 27.87. Additional SPF_2Cl (0.0071 g, 0.0521 mmol, 5.4%) was obtained as a result of the heating required to effect sublimation.

The powder, $Cl_2W(S_2PF_2)_3$, was slightly soluble in CS_2 but sparingly soluble in and reactive toward halogenated or protonic solvents.

(h) **With Tungsten Tetrachloride or Its Pyridine Adduct.**—At room temperature neither WCl_4 nor $WCl_4.2py$ reacted with F_2PS_2H; starting materials were recovered. At 70° similar results were obtained for $WCl_4 \cdot 2py$, but a *trace* of HCl contaminated with SPF_3, SPF_2Cl, and SiF_4 (ir spectrum) was obtained after 107 days in contact with WCl_4.

(i) **With Potassium Nonachloroditungstate(III).**—No reaction of $K_3[W_2Cl_9]$ with F_2PS_2H was observed at room temperature. At 100° (130 days) $K_3[W_2Cl_9]$ (0.3586 g, 0.436 mmol) and F_2PS_2H (0.7460 g, 5.56 mmol) reacted to yield a mixture of HCl and SPF_2Cl (0.1004 g), excess F_2PS_2H (0.5490 g), a trace of an unidentified volatile product which was trapped at −45°, and a brown, crystalline, involatile residue, which was identified by analysis as potassium heptachlorothioditungstate(III), $K_3[W_2Cl_7S]$ (0.326 g, 95%). *Anal.* Calcd for $Cl_7K_3SW_2$: Cl, 32.46; S, 4.19. Found: Cl, 33.16; S, 4.94. The product contained no $F_2PS_2^-$ ion or dithiophosphinate complex (ir spectrum). An aqueous solution of the product gave no lead sulfide on addition of lead nitrate. Readily soluble in water, the product was sparingly soluble in organic solvents.

(j) **With Molybdenum and Tungsten Metals.**—Neither molybdenum nor tungsten metal reacted with F_2PS_2H (20–100°) over lengthy periods. Slight decomposition of F_2PS_2H was noted at the elevated temperatures.

Results and Discussion

Reactions of Oxychlorides of Cr, Mo, and W.—It is interesting to note that the major product of the reaction of CrO_2Cl_2 with F_2PS_2H, $Cr[S_2PF_2]_3$, contains no oxygen whereas $OVCl_3$ gave both $V[S_2PF_2]_3$ and $OV[S_2PF_2]_2$.[3] All oxygen-containing products obtained from the CrO_2Cl_2 reaction were volatile: OPF_3, difluorophosphoric anhydride, $F_4P_2O_3$, and the oxy acid F_2PO_2H. In contrast to the CrO_2Cl_2 reaction, no oxygen abstraction occurred in the reactions of $OMoCl_4$ or $OWCl_4$ with F_2PS_2H, and no volatile oxygen-containing products were detected. This difference in reaction pathway illustrates the strongly oxygenating nature of chromyl chloride and the stability of the six-coordinate Cr(III) chelate complex.[2,4]

Difluorodithiophosphinic acid reacted smoothly and stoichiometrically with $OMoCl_4$ (although slowly, in contrast to the chromyl chloride reaction) to give HCl and equimolar amounts of $OMo(S_2PF_2)_2$ and $[F_2PS_2]_2$ in high yields according to eq 1. The latter product,

$$OMoCl_4 + 4F_2PS_2H \longrightarrow OMo(S_2PF_2)_2 + (F_2PS_2)_2 + 4HCl \qquad (1)$$

the "ligand dimer" $[F_2PS_2]_2$, is an expected product of oxidation–reduction reactions involving this acid.[17] The reaction of $OWCl_4$ was different, with only low yields of $OWCl(S_2PF_2)_2$ being obtained by a reaction summarized by eq 2. Notably the tungsten oxychloride was reduced

$$OWCl_4 + 3F_2PS_2H \longrightarrow OWCl(S_2PF_2)_2 + 3HCl + 0.5(F_2PS_2)_2 \qquad (2)$$

primarily to the pentavalent state, even under reflux conditions. Since yields were low it is possible that this product is only a minor product occluded in the major, involatile, lower valent reaction product when it was precipitated from the reaction mixture. Alternatively, this pentavalent tungsten compound may be the major product but is significantly decomposed during the sublimation process. As before, the major by-product was $(F_2PS_2)_2$, to be expected as a result of oxidation of $F_2PS_2^-$,[17] in approximately the expected amount for reduction of the metal to the pentavalent state. The small amounts of SPF_2Cl obtained could arise from a dissociation (eq 3).

$$OWCl(S_2PF_2)_2 \longrightarrow OW(S)S_2PF_2 + SPF_2Cl \qquad (3)$$

All of these reactions probably involve initial substitution of chloride by a monodentate $F_2PS_2^-$ ion ligand followed by chelation with elimination of $(F_2PS_2)_2$ in a reduction step. Both oxygen and chloride substitutions are easy in the Cr case; however, even chloride substitution is difficult to effect in tungsten oxychloride.

Reactions of Simple Chlorides of Mo and W.—Either $MoCl_5$ or $MoCl_4$ was reduced by F_2PS_2H to yield $Mo(S_2PF_2)_3$ (eq 4), the former far more readily

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[17] H. W. Roesky and M. Dietl, *Z. Naturforsch. B*, **24**, 1243 (1969).

TABLE II

VIBRATIONAL SPECTRA[a]

$Cr(L_F)_3$[4,f]	$Mo(L_F)_3$[b]	$OMo(L_F)_2$		$OWCl(L_F)_2$	Residue[f,g]	$Cl_2W(L_F)_3$[f]	
Ir[c]	Ir[d]	Ir[d]	Raman[e]	Ir[c]	Ir[c]	Ir[c]	Assignment
				1218 (vw)	1253 (br, w)		
				1153 (w)	1143 (m)	1153 (w)	
				1083 (vw)	1022 (vw)	1080 (w)	
		1006 (m)					ν(M–O)
				991 (w)	955 (w, sh)		
901 (vs)				923 (s, sh)		914 (sh)	$\nu(PF_2)$[h]
897 (vs)	893 (vs)	886 (vs)		905 (vs)	895 (br, vs)	896 (br, s)	$\nu_{sym}(PF_2)$
863 (vw)				857 (m, sh)		878 (sh)	$\nu(PF_2)$[h]
			852 (vs)				$\nu_{as}(PF_2)$
708 (s)				717 (w)	722 (vw)	722 (w)	$\nu_{as}(PS_2)$
698 (m)	695 (s)	700 (s)	703 (w)	693 (m)	694 (m)	698 (m)	$\nu_{sym}(PS_2)$
560 (w)	546 (vw)	540 (vw)	542 (m)	550 (vw)	554 (vw)	556 (vw)	ν(PS)
				522 (vw)	523 (vw)	535 (w)	
			466 (w)				
404 (m)	402 (w)	403 (w)	403 (w)	404 (w)	407 (w)	407 (w)	$\nu(M–S_n)$
	354 (w)	342 (w)					
		339 (w)		339 (vw)		341 (w)	
	307 (w)	306 (w)	309 (sh)			304 (w)	
	297 (w)	293 (sh)	298 (m)				
		286 (w)		283 (w)	297 (bvw)	280 (w)	
		270 (w)	257 (w)				
			235 (w)				
			220 (sh)				

[a] $L_F = F_2PS_2^-$, br = broad, m = medium, s = strong, sh = shoulder, v = very, w = weak. All values in cm^{-1}. [b] Vaporized by red laser beam. [c] "Nujol" mull. [d] Solution (CS_2) spectrum (4000–400 cm^{-1}), "Nujol" mull (550–100 cm^{-1}). [e] Green laser. [f] No Raman spectrum on any laser line; intense color and readsorption of emitted photons. [g] Residue from sublimation of $OWCl(L_F)_2$. [h] Monodentate F_2PS_2 assignment.

$$2MoCl_n + 2nF_2PS_2H \longrightarrow 2Mo(S_2PF_2)_3 + (n-3)(F_2PS_2)_2 \quad (n = 4, 5) \qquad (4)$$

than the latter. Again the tungsten chlorides were less reactive than the molybdenum chlorides; only WCl_6 reacted with F_2PS_2H to give the $Cl_2W(S_2PF_2)_3$ complex with incomplete replacement of chloride being obtained (eq 5). The lower valent tungsten chlorides

$$WCl_6 + 4F_2PS_2H \longrightarrow WCl_2(S_2PF_2)_3 + 3HCl + SPF_3 + SPF_2Cl, \text{ etc.} \qquad (5)$$

WCl_4 and $WCl_4 \cdot 2py$ did not react with the acid and no evidence for a W(IV) complex was obtained in the reaction products of WCl_6. The tungsten sulfides which remained as the residues following sublimation of the crude $Cl_2W(S_2PF_2)_3$ may have been formed by the reaction sequence

$$WCl_6 + 3F_2PS_2H \longrightarrow Cl_3W(S_2PF_2)_3 + 3HCl \qquad (6)$$

$$Cl_3W(S_2PF_2)_3 \longrightarrow 3SPF_2Cl + WS_3 \qquad (7)$$

Reduction may occur during the reaction or during fractionation and sublimation.

The Mo(III) complex, K_3MoCl_6, did not react with F_2PS_2H; however, the tungsten(III) complex, $K_3W_2Cl_9$, reacted with a stoichiometry which is probably 1:1, but partial decomposition of F_2PS_2H during the period of the reaction (130 days, 100°) precluded accurate assay of the volatile products. Readily soluble in water but sparingly soluble in organic solvents, the crystalline product was indicated by analysis to be the novel complex $K_3[W_2Cl_7S]$. No sulfide ion was present, as shown by the lack of reaction with aqueous lead nitrate. It is reasonable to suppose that chloride replacement to give $W_2Cl_8(S_2PF_2)^{3-}$ occurs initially (eq 8) followed by thermal decomposition of the ion to

$$K_3[W_2Cl_9] + HS_2PF_2 \longrightarrow K_3[W_2Cl_8S_2PF_2] + HCl \qquad (8)$$

the $W_2Cl_7S^{3-}$ according to eq 9. Since the $R_2PS_2^-$ ion

$$K_3[W_2Cl_8S_2PF_2] \xrightarrow{\Delta} K_3[W_2Cl_7S] + SPF_2Cl \qquad (9)$$

is known to act as a bridging ligand,[18-22] it is possible that the initial reaction (eq 8) involves displacement of *bridging* chloride by bridging $F_2PS_2^-$, with subsequent formation of the *bridging* thio complex (eq 9) by thermal decomposition.

Vibrational Spectra.—The P–F stretching modes for $OMo(S_2PF_2)_2$ and the tungsten-containing residue obtained from the $OWCl_4$ reaction were single bands (886 and 895 (br) cm^{-1}, respectively) indicating that the ligand $F_2PS_2^-$ is chelating.[2,8,9] Similarly, a single band was observed for the P–S stretching modes (700 and 694 cm^{-1}, respectively), but a weak band (722 cm^{-1}) was also observed in the latter case. However, for $OWCl(S_2PF_2)_2$, three P–F stretching modes were observed (923, 905, and 857 cm^{-1}) indicating the presence of both monodentate and chelating $F_2PS_2^-$ ligands.[2,8,9] The band at 857 cm^{-1} in $OWCl(S_2PF_2)_2$ is probably $\nu_{asym}(PF_2)$, corresponding to the band at 852 cm^{-1} (observed in the Raman only) for $OMo(S_2PF_2)_2$, while the band at 905 cm^{-1}, corresponding to the band at 886 cm^{-1} (observed in the infrared only) for $OMo(S_2PF_2)_2$, is probably $\nu_{sym}(PF_2)$. The band at 923 cm^{-1} is probably $\nu(PF_2)$ for monodentate $F_2PS_2^-$.

For $OMo(S_2PF_2)_2$ ν(MoO) is observed as a medium band (1006 cm^{-1}) in solution, but only as a very weak band in the solid ("Nujol" mull). This confirms that $OMo(S_2PF_2)_2$ is monomeric in solution, as indicated by the molecular weight in CH_2Br_2, but suggests that it is associated in the solid state, probably with an Mo–O

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(18) M. J. Bennett and R. H. Sumner, unpublished results.

(19) M. Calligaris, G. Nardin, and A. Ripamonti, *J. Chem. Soc. A*, 714 (1970).

(20) M. Calligaris, A. Ciana, S. Meriani, G. Nardin, L. Randaccio, and A. Ripamonti, *J. Chem. Soc. A*, 3386 (1970).

(21) S. L. Lawton, *Inorg. Chem.*, **10**, 328 (1971).

(22) T. Ito, T. Igarashi, and H. Hagihara, *Acta Crystallogr., Sect. B*, **25**, 2303 (1969).

linked chain structure. The linkage within the chain is weak, as the complex showed no polynuclear species in the mass spectrum, sublimed readily at low temperatures, and was readily soluble in organic solvents.

Neither the tungsten complex, $OWCl(S_2PF_2)_2$, nor the residue sublimed at low temperatures or was readily soluble in organic solvents, and both showed dinuclear moieties in the mass spectrum indicating that they are polymeric, with strong W—O linked chain structures. The multiplicity of weak bands at 955–1253 cm^{-1} ("Nujol" mulls) precluded positive assignment of a W—O stretching mode. The possibility of a bridging $F_2PS_2^-$ structure, with terminal W=O bonds, or a dimeric structure with a W_2O_2 ring linkage is excluded, as either would be expected to show a characteristic, strong W—O stretching absorption.

The single bands observed in the ir spectrum of $Mo(S_2PF_2)_3$ at 893 cm^{-1} ($\nu_{sym}(PF_2)$) and 695 cm^{-1} ($\nu_{sym}(PS_2)$) are indicative that $F_2PS_2^-$ is present only as a chelating ligand.[2,8,9] As for $OMo(S_2PF_2)_2$ no band which could be assigned to $\nu_{asym}(PF_2)$ was observed in the ir spectrum. Unfortunately, attempts to obtain Raman spectra were unsuccessful, because the sample sublimed away from the laser beam. Thus no further comparison can be made at this time.

For $Cl_2W(S_2PF_2)_3$ three strong bands (919, 901, 881 cm^{-1}) and a weak band (832 cm^{-1}) are assigned as P–F stretching modes. Two bands (723, 698 cm^{-1}) are assigned as P–S stretching modes. This is consistent with the presence of $F_2PS_2^-$ as both a monodentate and chelating ligand. No Raman spectrum was observed because of the readsorption of emitted photons by the intensely colored complex. The bands (919, 881 cm^{-1}) are assigned as $\nu_{sym}(PF_2)$ and $\nu_{asym}(PF_2)$, respectively, for the chelating ligand.

Mass Spectra.—For either $OMo(S_2PF_2)_2$ or $OWCl(S_2PF_2)_2$ the parent (monomer) ion was observed, and the former was mass measured. The mass spectrum of the tungsten residue showed $[OW(S_2PF_2)_2]^+$ but not $[OWCl(S_2PF_2)_2]^+$. A number of dinuclear moieties were observed for both tungsten-containing samples; up to $[W_2(S_2PF_2)_2O_2S_2]^+$ and $[W_2(S_2PF_2)_3O_2S]^+$ arise for $OWCl(S_2PF_2)_2$ and the residue, respectively. The former may arise by elimination of SPF_2Cl

$$2OWCl(S_2PF_2)_2 \longrightarrow 2SPF_2Cl + [W_2O_2S_2(S_2PF_2)_2] \quad (10)$$

No peaks for *m/e* greater than the pattern for the parent ion were observed for $OMo(S_2PF_2)_2$, illustrating the comparative ease of breaking of the O–Mo linked chain structure.

For $Mo(S_2PF_2)_3$ the parent ion (mass measured) and all expected fragments were observed. For $Cl_2W(S_2PF_2)_3$ no parent ion was observed, an apparent parent ion $(S_2WS_2PF_2)_2^+$ being detected instead. This could arise by elimination of SPF_2Cl in an analogous manner to reactions 7 or 9. Apart from SPF_2Cl^+, fragments thereof, and weak peaks for WCl^+, $WSCl^+$, etc., no chlorine-containing fragments were observed.

Magnetic Measurements.—Diamagnetic in the solid state, $OMo(S_2PF_2)_2$ also shows no epr resonance in solution. The ^{19}F nmr spectrum in pyridine solution showed only a sharp doublet (ϕ_F +1.9 ppm relative to $CFCl_3$, J_{FP} = 1121 cps) indicating the presence of $F_2PS_2^-$ in pyridine solution. In solution in CS_2–$CFCl_3$ a weak, broad doublet at high chemical shift was observed, indicating that a paramagnetic, species may be present.

The magnetic moment of $Mo(S_2PF_2)_3$ (3.53 BM) is temperature independent, showing no evidence for strong metal–metal interaction. The temperature-dependent susceptibility is given in Table III. The observed moment is lower than the spin-only value due to a significant negative contribution from spin–orbit coupling, as expected.[23] No epr resonance was observed, as expected for a d^3 system, because of relaxation processes.

TABLE III

MAGNETIC SUSCEPTIBILITY OF $Mo(S_2PF_2)_3$

T, °K	$10^3\chi_M$ (obsd)	T, °K	$10^3\chi_M$ (obsd)
298.0	5.01	168.3	8.56
278.0	5.28	149.6	9.69
252.8	5.84	129.1	11.15
223.2	6.66	110.8	12.06
194.0	7.51	88.4	15.26

Electronic Spectra. (a) **$Mo(S_2PF_2)_3$.**—On a model of approximately O_h symmetry three spin-allowed d–d transitions are expected,[24] of which $\nu_3(^4T_1(P) \leftarrow {}^4A_2)$ is generally submerged under charge-transfer or intraligand transitions in the near-uv. This has proved the case. The transitions $\nu_1(^4T_2 \leftarrow {}^4A_2)$ and $\nu_2(^4T_1(F) \leftarrow {}^4A_2)$ are observed (see Table IV), but the transition ν_3, calculated to occur approximately at 41,900 cm^{-1}, is submerged beneath two intense bands. The Racah repulsion parameter (B') is calculated to be 390 cm^{-1}. This is approximately 60% of the free ion value,[24] indicating considerable electron delocalization. This is in good agreement with recent results for the analagous chromium(III) complex[4,25] which yields a value of 445 cm^{-1} for the interelectronic repulsion parameter B' (49% of the value for the free ion). This value indicates that $F_2PS_2^-$ has a slightly lower nephelauxetic character than the analogous ligands $R_2PS_2^-$ (R = alkyl), but in all of the dithiophosphinate complexes considerable electron delocalization occurs. The splitting[4] of the transitions ν_1 and ν_2 observed in $Cr(S_2PX_2)_3$ complexes is not observed in the spectrum of $Mo(S_2PF_2)_3$. It now appears that these additional features observed in the Cr(III) complexes[4] may be

TABLE IV

ELECTRONIC SPECTRA[a]

$Mo(S_2PF_2)_3$		$OMo(S_2PF_2)_2$	
$10^{-3}\nu_{max}$, cm^{-1}	ϵ[b]	$10^{-3}\nu_{max}$, cm^{-1}	ϵ[b]
42.42[c]	16,758	44.87[c]	2751
35.11[c]	5,278	40.62[c]	3644
30.72[c]	4,993	37.78[c]	1211
24.31[e]	99.3	32.84[d]	105
20.02[f]	204.8	28.87[d]	43.8
		24.56[d]	52.4
		19.98[d]	86.6

[a] Analyzed employing the program BIGAUSS; see ref 4. [b] Molar extinction coefficient ϵ of absorption maximum ν_{max}. [c] Charge-transfer or intraligand transitions. [d] Unassigned d–d transitions. [e] $^4T_1(F) \leftarrow {}^4A_2$. [f] $^4T_2 \leftarrow {}^4A_2$.

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(23) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966.

(24) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1968.

(25) C. K. Jørgensen, *Inorg. Chim. Acta Rev.*, **2**, 65 (1968).

better[26] assigned as the three spin-forbidden transitions, $^2E_g(G) \leftarrow {}^4A_{2g}(F)$, $^2T_{1g}(G) \leftarrow {}^4A_{2g}(F)$, and $^2T_{2g}(G) \leftarrow {}^4A_{2g}(F)$, although conclusions based on extraction of low-intensity components of absorption bands by Gaussian analysis procedures must be considered tenuous. Initial single-crystal spectroscopic studies[27] on a chromium(III) dithiophosphinate complex have not completely solved the problem and further study is warranted.

(b) **$OMo(S_2PF_2)_2$.**—Three intense charge-transfer or intraligand transitions dominate the high-energy part of the spectrum and may mask one or more d–d transitions. Four d–d transitions are observed, but unambiguous assignment of the bands awaits a full determination of the symmetry of the system (probably C_{2v}) and calculation of spectral parameters.

Conclusions

Chlorides and oxychlorides of chromium, molybdenum, and tungsten in their higher valence states react readily with F_2PS_2H to yield novel difluorodithiophosphinato complexes of the metals in reduced valence states. Whereas oxygen abstraction from O_2CrCl_2 readily occurs, no parallel reaction occurs for $OMCl_4$ (M = Mo, W), and reduction of the central metal atom occurs by elimination of $(F_2PS_2)_2$ instead. The reactivity of the metal chlorides decreases rapidly with reduction in the valence state of the central metal atom. Reduction and reaction were most facile for chromium and least facile for tungsten.

Aerial oxidation of $Mo(S_2PF_2)_3$ gave $OMo(S_2PF_2)_2$. In contrast to the reactions of pyridine or acetonitrile with $Cl_3M(S_2PF_2)_2$ (M = Nb, Ta),[28] the complex $Mo(S_2PF_2)_3$ was recovered unchanged from solution in pyridine or nonpolar organic solvents, while $OMo(S_2PF_2)_2$ gave the ionic complex $[OMo \cdot 4py]^{2+}(S_2PF_2)_2^-$.

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[26] E. D. Day, Ph.D. Thesis, University of Alberta, 1972.

[27] A. A. G. Tomlinson, *J. Chem. Soc. A*, 1409 (1971).

[28] R. G. Cavell and A. R. Sanger, *Inorg. Chem.*, **11**, 2016 (1972).

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Metal Complexes of Substituted Dithiophosphinic Acids. VII. Reactions of $TiCl_4$, VCl_4, $NbCl_4$, $NbCl_5$, and $TaCl_5$ with Difluorodithiophosphinic Acid

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The reactions of difluorodithiophosphinic acid, F_2PS_2H, with MCl_5 (M = Nb, Ta), $NbCl_4$, or $TiCl_4$ gave the chloro(difluorodithiophosphinato) complexes $Cl_3M(S_2PF_2)_2$, $Cl_3NbS_2PF_2$, or $Cl_3TiS_2PF_2$, respectively, while VCl_4 affords the known complex $V(S_2PF_2)_3$; neither niobium nor tantalum metal formed complexes by reaction with F_2PS_2H. Pyridine reacts with $Cl_3Nb(S_2PF_2)_2$ to give SPF_3 and a pyridine–chlorothioniobium(V) complex and with $Cl_3Ta(S_2PF_2)_2$ to give an adduct and no SPF_3.

Introduction

The reaction of the recently discovered strong acid F_2PS_2H[1] with metals,[2-4] metal oxide (Ag),[2] or metal halides[2-4] results in the formation of difluorodithiophosphinate complexes. We have also been studying other disubstituted dithiophosphinates of the transition metals,[3,4] and a number of organometallic difluorodithiophosphinates have also been prepared.[5,6] We now report the reactions of F_2PS_2H with the pentachlorides of niobium and tantalum, the tetrachlorides of niobium, vanadium, and titanium, and the metals niobium and tantalum.

Results and Discussion

The pentachlorides of niobium and tantalum reacted readily with 2 mol of F_2PS_2H[1] to give 2 mol of HCl and thermally stable, air- and moisture-sensitive, volatile, crystalline complexes of the metals in their original pentavalent states (eq 1). The complexes were in-

$$MCl_5 + 2HS_2PF_2 \longrightarrow Cl_3M(S_2PF_2)_2 + 2HCl \qquad (1)$$
$$(M = Nb, Ta)$$

sufficiently soluble or stable in appropriate solvents to enable the determination of molecular weight or conductivity data in solution. The complexes were diamagnetic, as expected for the pentavalent (d^0) systems, and as expected no epr signals were detected.

The infrared spectra (Table I) show the P–S stretching modes close together in the range 723–700 cm^{-1} and the P–F stretching modes close together in the range 916–907 cm^{-1}, indicating that both $F_2PS_2^-$ ligands in each complex are complexing and bidentate.[2-5] No bands associated with the free ion $F_2PS_2^-$ were observed.[6] The number of bands in the infrared spectrum which can be assigned to metal–sulfur, metal–chlorine, or skeletal vibrational modes is indicative of low symmetry about the central metal atom.

The volatility of the complexes and the mass spectral fragmentation patterns indicate the presence of molecular structures, of the formula $Cl_3M(S_2PF_2)_2$, although no parent ions were observed. Each set of peaks associated with the loss of one ligand, [parent − Cl]$^+$ or

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[1] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 281 (1969); R. W. Mitchell, M. Lustig, F. A. Hartman, J. K. Ruff, and J. A. Merritt, *J. Amer. Chem. Soc.*, **90**, 6319 (1968).

[2] F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, **9**, 629 (1970).

[3] (a) R. G. Cavell, E. D. Day, W. Byers, and P. M. Watkins, *ibid.*, **10**, 2716 (1971); (b) *ibid.*, **10**, 2710 (1971); (c) unpublished results.

[4] R. G. Cavell, E. D. Day, P. M. Watkins, and W. Byers, *Inorg. Chem.*, **11**, 1591, 1598, 1759 (1972).

[5] J. K. Ruff and M. Lustig, *Inorg. Chem.*, **7**, 2171 (1968).

[6] M. Lustig and J. K. Ruff, *ibid.*, **6**, 2115 (1967).