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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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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TABLE I

VIBRATIONAL SPECTRA OF THE COMPLEXES $Cl_3M(S_2PF_2)_2$ (M = Nb, Ta)

$Cl_3Nb(S_2PF_2)_2$		$Cl_3Ta(S_2PF_2)_2$		
Infrared[a]	Raman[b,c]	Infrared[a]	Raman[c]	
914 (vs)	919	916 (vs)		ν(P–F)
907 (sh)		907 (sh)		
	890			
722 (w, sh)		723 (w, sh)		
713 (w, sh)		709 (s)	708	ν(P–S)
701 (m)		700 (sh)	698	
	690			
	564		567	
556 (w)		558 (w)		$\delta(PF_2)$
517 (vw)		518 (vw)		
402 (w)		406 (w)		
380 (w)		385 (vw)		
356 (w)			363	
	347		354	
340 (vw)		345 (br)		
275 (br)		284 (w)		
? (vw)	219		227?	
? (vw)		206 (vw)		
		186 (vw)		
	157	159 (w)	160	
149 (vw)		140 (vw)		
		123 (w)		
		117 (w)		
			80	

[a] Solution (CS_2) 4000–400 cm^{-1}, solid sample ("Nujol" mull) 400–50 cm^{-1}. [b] Fluoresced initially; subsequently afforded this spectrum. [c] Yellow laser.

$[\text{parent} - S_2PF_2]^+$ [mass measured, found *m/e* 330.7274 (calcd for $^{35}Cl_3Nb(S_2PF_2)$, 330.7279); found *m/e* 418.7696 (calcd for $^{35}Cl_3Ta(S_2PF_2)$, 418.7693)], is observed. The peaks $[\text{parent} - S_2PF_2]^+$ are an order of magnitude stronger than the peaks $[\text{parent} - Cl]^+$ for each complex, possibly because of the low stability of the parent seven-coordinate structure assuming that both dithiophosphinate ligands are chelating. The fragmentation patterns and ion-intensity distributions for each complex are similar. The major difference is the appearance for the case of $Cl_3Nb(S_2PF_2)_2$ only of the ion $ClNb(S_2PF_2)_2$, $[\text{parent} - 2Cl]^+$.

The small amounts of SPF_2Cl in the volatile products of the reaction of $NbCl_5$ with F_2PS_2H may arise by a further reaction

$$Cl_3Nb(S_2PF_2)_2 \longrightarrow Cl_2Nb(S)S_2PF_2 + SPF_2Cl \qquad (2)$$

Similar behavior has been observed during the sublimation of the tungsten complex, $Cl_2W(S_2PF_2)_3$.[7] The trace of green product found in the $NbCl_5$ reaction may be the complementary product of such a reaction.

The ^{19}F nmr spectrum of a saturated solution (CS_2–$CFCl_3$) of $Cl_3Nb(S_2PF_2)_2$ was composed of a strong central doublet (separation 1298 Hz), with additional weak lines due to second-order splitting by long-range couplings to F and P. The chemical shift (ϕ_F +19.55 ppm *vs.* $CFCl_3$) is the second highest yet recorded for a transition metal difluorodithiophosphinate, being slightly lower than the value for $Cl_3TiS_2PF_2$ (see below). The magnitude of the doublet separation (which is actually $^1J_{FP} + {}^5J_{FP}$ of an $X_2AA'X'_2$ system[8] although it has been assigned elsewhere[2] as $^1J_{PF}$) is consistent with $F_2PS_2^-$ as a chelating ligand.[2,5,9]

On dissolution in and reaction with pyridine, $Cl_3Nb(S_2PF_2)_2$ slowly deposited paramagnetic, green crystals and evolved SPF_3. The green crystals contained no $F_2PS_2^-$ complex but did contain pyridine (ir spectrum). The complex, analysis of which agrees with $C_{30}H_{34}Cl_{11}N_6Nb_3S_3$, was possibly formed according to eq 3 and 4, the Cl_2NbS and pyridinium chloride or 1-(4-pyridyl)pyridinium dichloride being formed by reduction of Cl_3NbS or $Cl_3Nb(S_2PF_2)_2$, as previously postulated to explain their formation in the reductions of $NbCl_5$ and $TaCl_5$ with pyridine to the $MCl_4 \cdot 2py$ complexes.[10,11]

$$3ClNb(S_2PF_2)_2 \longrightarrow 3Cl_3NbS + 4SPF_3 + P_2S_5 \qquad (3)$$

$$Cl_3NbS + 2Cl_2NbS + 4pyHCl + 2py \longrightarrow [pyH]_4{}^+[S_3Nb_3Cl_{11}] \cdot 2py^{4-} \qquad (4)$$

In contrast, pyridine did not liberate SPF_3 from $Cl_3Ta(S_2PF_2)_2$; instead the tantalum complex dissolved to form a brown solution, from which an orange-brown tarry solid was obtained. The solid appeared to be a pyridine complex of tantalum, containing no $F_2PS_2^-$ ligand.

The reaction of $NbCl_4$ with F_2PS_2H evolved no more than 1 mol of HCl, even under reflux conditions, and no other volatile product was detected, thus indicating that the reaction followed the stoichiometry indicated in eq 5. Heating the resultant brown solid gave a low

$$NbCl_4 + F_2PS_2H \longrightarrow Cl_3NbS_2PF_2 + HCl \qquad (5)$$

yield of $Cl_4Nb_2(S_2PF_2)_5$ as an ocher sublimate. The mass spectrum of the ocher sublimate was similar to that of $Cl_3Nb(S_2PF_2)_2$, with the notable presence of a weak set of peaks (*m/e* 527–531) assignable as $[ClNb(S_2PF_2)_3]^+$ and much more intense peaks for diniobium moieties.

The reaction of VCl_4 with F_2PS_2H (eq 6) afforded

$$2VCl_4 + 8F_2PS_2H \longrightarrow 2V(S_2PF_2)_3 + 8HCl + (F_2PS_2)_2 \qquad (6)$$

only HCl, $(F_2PS_2)_2$, and red crystals, which were identified as $V(S_2PF_2)_3$ by comparison of infrared and mass spectra (including mass-measured parent ion) with those of an authentic sample.[3a] The large crystals so obtained were free from contaminating $VO(S_2PF_2)_2$ even without sublimation. In contrast, the reaction of $VOCl_3$ with F_2PS_2H gave a mixture of the reduction products $VO(S_2PF_2)_2$ and $V(S_2PF_2)_3$.[3a] The latter product is also readily prepared by the reaction of VCl_3 with F_2PS_2H.[3a] Thus eq 6 is a more convenient synthetic route to this complex. No eight-coordinate complex, corresponding to the dithiocarbamates $V(S_2CNR_2)_4$,[12] was isolated.

The reaction of $TiCl_4$ and F_2PS_2H in equimolar amounts, with the liberation of approximately 1 mol of HCl per mole of $TiCl_4$, indicates that the stoichiometry of the reaction is as shown

$$TiCl_4 + F_2PS_2H \longrightarrow Cl_3TiS_2PF_2 + HCl \qquad (7)$$

The ^{19}F nmr spectrum of the yellow liquid product ($CFCl_3$ solution) showed only a sharp doublet (ϕ_F 19.7 ppm *vs.* $CFCl_3$; J_{FP} = 1283 Hz) with no further splitting and no broadening due to paramagnetic species. This is consistent with a single $F_2PS_2^-$ as a chelating ligand,[2,5,9] and with a titanium(IV) complex. The

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TABLE II

REACTIONS OF F_2PS_2H WITH MCl_4 (M = Ti, V, Nb) AND MCl_5 (M = Nb, Ta)

Reagent	$F_2PS_2H^a$ consumed	HCl^a	Product	Color	Subl temp,^{b} °C	Mp,^{c} °C	By-products
$TiCl_4$	1.05	1.2	$Cl_3TiS_2PF_2$	Orange		Liquid	
VCl_4			$V(S_2PF_2)_3$	Red		42–43	$(F_2PS_2)_2$
$NbCl_4$	~1.0	0.86	$Cl_3NbS_2PF_2$	Brown	Dec >100		
$NbCl_5$	≥2.0	2.0	$Cl_3Nb(S_2PF_2)_2^d$	Orange^e	70–90	147–150 dec	SPF_2Cl, (trace)
$TaCl_5$	≥2.0	2.2	$Cl_3Ta(S_2PF_2)_2^d$	Yellow	70–90	150.5	

[a] Molar ratio. [b] Under vacuum (10^{-4} mm). [c] Sealed capillaries; uncorrected. [d] Diamagnetic. [e] Major product; trace of green material also obtained.

mass spectrum showed major peaks only for the elements and fragments of the ligand $F_2PS_2^-$. The low volatility of the complex and its sensitivity to air and many solvents have precluded elemental analyses and made further study of its properties difficult. However, surprisingly no complex corresponding to the analogous $[CH_3(F)PS_2]_2TiCl_2$[13] was formed.

Experimental Section

The reagents F_2PS_2H,[1] $NbCl_5$,[14] $NbCl_4$,[15,16] and $TaCl_5$[16,17] 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-atmosphere techniques. Analyses were performed by the analytical service of the Department of Chemistry, University of Alberta, Edmonton, or at the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Spectra were obtained 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 moments were obtained using the Faraday method, on a balance constructed in this laboratory.[3] The reactions, detailed below, are summarized in Table II.

Reaction of F_2PS_2H with (a) Tantalum Pentachloride.—In a typical experiment, freshly sublimed tantalum pentachloride (0.313 g, 0.873 mmol) and F_2PS_2H (1.385 g, 10.33 mmol) were mixed at −196° in a reaction tube, which later served as a sublimator for isolation of the product. The mixture was allowed to warm slowly to room temperature. At temperatures greater than −20° dissolution into, and reaction of, the halide with F_2PS_2H occurred. Within 10 min a fine yellow precipitate was deposited. The mixture was allowed to stand (12 hr) to ensure complete reaction, and the mixture was subsequently vacuum fractionated to yield HCl (0.071 g, 1.94 mmol), excess F_2PS_2H (1.017 g), and yellow solid. Heating (70–90° (10^{-4} mm)) the solid gave, as a yellow, diamagnetic, crystalline sublimate, trichlorobis(difluorodithiophosphinato)tantalum(V) (0.375 g, 77%), mp 150.5°. *Anal.* Calcd for $Cl_3F_4P_2S_4Ta$: Cl, 19.05; F, 13.73; S, 23.18. Found: Cl, 19.29; F, 14.05; S, 23.40. An unidentified brown residue (0.015 g) remained in the sublimation apparatus. Under reflux conditions (~70°) similar results were obtained.

Pyridine (2 ml) dissolved trichlorobis(difluorodithiophosphinato)tantalum(V), $Cl_3Ta(S_2PF_2)_2$ (0.155 g, 0.028 mmol), to form a brown solution. After standing (12 hr) the mixture was fractionated to yield pyridine as the only volatile component plus a brown solid mass. The mass was dried (3 weeks, 25° (10^{-4} mm)) to yield an orange-brown tarry solid, identified as a pyridine complex of tantalum, containing no $F_2PS_2^-$ ligand according to the ir spectrum.

In acetonitrile $Cl_3Ta(S_2PF_2)_2$ dissolved to form an orange solution. Removal of excess acetonitrile under reduced pressure gave an orange-brown acetonitrile complex, which has not yet been unambiguously identified. In $CFCl_3$, CH_2Cl_2, or $CHCl_3$, $Cl_3Ta(S_2PF_2)_2$ was sparingly soluble and unstable, and with ethanol or water it reacted with destruction of the complex.

(b) **Niobium Pentachloride.**—In a typical experiment freshly sublimed niobium pentachloride (0.208 g, 0.767 mmol) and F_2PS_2H (1.236 g, 9.22 mmol) were mixed and allowed to react as described above. Vacuum fractionation of the reaction mixture gave HCl (0.052 g, 1.433 mmol), excess HS_2PF_2 (0.937 g), contaminated with a little SPF_2Cl (ir spectrum), and an orange solid. Heating (70–90° (10^{-4} mm)) the solid afforded a trace (usually none) of an unidentified green powder and an orange, diamagnetic, crystalline sublimate identified as trichlorobis(difluorodithiophosphinato)niobium(V) (0.261 g, 73%), mp 147–150° dec. *Anal.* Calcd for $Cl_3F_4NbP_2S_4$: Cl, 22.88; F, 16.33; Nb, 19.96; S, 27.55. Found: Cl, 22.47; F, 16.03; Nb, 19.86; S, 27.03. Under reflux conditions (~70°) similar results were obtained.

Pyridine (1 ml) dissolved trichlorobis(difluorodithiophosphinato)niobium(V) (0.055 g, 0.0119 mmol) to form initially a blood red solution which became green within 1 min. Within 1 hr at 25° dark green crystals were formed. After standing (1 day) the paramagnetic ($\mu_{eff} \sim 2.2$ BM at 298°) crystals (~8 mg) were separated. The infrared spectrum showed the absence of the $F_2PS_2^-$ ligand; however, pyridine was present. Analysis of the crystals indicated that a reasonable formulation of the product as a trinuclear chloro(pyridine) complex of niobium, $[pyH]_4{}^+[S_3Nb_3Cl_{11}]^{4-}\cdot 2py$, gave fair agreement with results. *Anal.* Calcd for $C_{30}H_{34}Cl_{11}N_6Nb_3S_3$: C, 28.98; H, 2.74; Cl, 31.38; S, 7.75. Found: C, 29.78; H, 2.72; Cl, 33.28; S, 8.22.

After the reaction had been allowed to proceed for 7 days at room temperature, the fractionated volatile components were identified as SPF_3 (3.3 mg, 0.0275 mmol, 2.3 equiv) and pyridine. A brown mass remained in the reactor tube from which no pure product has been isolated.

Similarly, $Cl_3Nb(S_2PF_2)_2$ dissolved in acetonitrile to form a deep green solution. After standing (4 days), volatiles were removed under reduced pressure to afford a brown solid which can be similarly characterized as a polynuclear chloro(difluorodithiophosphinato)(acetonitrile) complex of niobium by analysis. *Anal.* Calcd for $Cl_5Nb_2(S_2PF_2)_4\cdot 7MeCN$: C, 14.23; H, 1.79; Cl, 14.79; S, 21.69. Calcd for $Cl_5Nb(S_2PF_2)_4\cdot 8MeCN$: C, 15.69; H, 1.98; Cl, 14.47; S, 20.93. Calcd for $Cl_6Nb_3(S_2PF_2)_5\cdot 9MeCN$: C, 14.16; H, 1.78; Cl, 13.95; S, 20.98. Found: C, 14.55; H, 2.24; Cl, 13.83; S, 20.19.

In $CFCl_3$, CH_2Cl_2, or $CHCl_3$, $Cl_3Nb(S_2PF_2)_2$ was sparingly soluble and unstable, and with water it was hydrolyzed slowly.

(c) **Niobium Tetrachloride.**—In a typical reaction niobium tetrachloride (0.2195 g, 0.935 mmol) and F_2PS_2H (excess) were mixed and allowed to react as described above. The mixture was refluxed (2 days) and the golden-brown solution was subsequently fractionated to afford HCl (0.0294 g, 0.807 mmol) and excess F_2PS_2H as the only volatile products, and a brown solid, probably containing trichloro(difluorodithiophosphinato)niobium(IV). Heating (90–100° (10^{-4} mm)) the solid for 4 hr gave only a dull ocher sublimate in low yield, possibly of $Cl_4Nb_2(S_2PF_2)_5$ (5.56 mg). *Anal.* Calcd for $Cl_4F_{10}Nb_2P_5S_{10}$: Cl, 14.27; S, 32.30. Found: Cl, 14.60; S, 32.80. However, on repeating the experiment, a lighter colored sublimate, possibly $Cl_3NbS_2PF_2$, was obtained in low yield at a lower temperature. *Anal.* Calcd for $Cl_3F_2NbPS_2$: S, 19.25. Found: S, 19.24.

(d) **Vanadium Tetrachloride.**—Vanadium tetrachloride, purified by trap-to-trap distillation in an all-glass apparatus, and excess F_2PS_2H were mixed and allowed to react as described above. At about −20° the mixture was a purple solution, at 0° it was brown, and after 1 min at room temperature it was blood red. The mixture was fractionated to afford HCl, excess

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F_2PS_2H, $(F_2PS_2)_2$, and, as red crystals, tris(difluorodithiophosphinato)vanadium(III).[3a]

(e) **Titanium Tetrachloride.**—Titanium tetrachloride (0.2104 g, 1.11 mmol) and F_2PS_2H (0.5413 g, 4.04 mmol) were mixed and allowed to react as described above. The mixture slowly darkened to a red-orange solution. After standing (1 day) the mixture was fractionated to afford HCl (0.049 g, 1.34 mmol), excess F_2PS_2H (0.3859 g; consumed, 0.1554 g, 1.16 mmol) and an orange liquid, probably trichloro(difluorodithiophosphinato)titanium(IV), of very low volatility. Repeating the reaction over 7 weeks or at 70° (1 day) afforded similar results. The liquid was sufficiently volatile to enable small amounts to be transferred (~2 days, 25° (10^{-4} mm)) to a break-seal for mass spectrometric or to an nmr tube for ^{19}F nmr characterization of the product.

(f) **Niobium or Tantalum Metal.**—Niobium metal did not react (25–70°, 100 days) with F_2PS_2H. Tantalum metal did not react at room temperature with F_2PS_2H but at 70° (140 days) catalyzed the decomposition of F_2PS_2H to P_2S_5 and a mixture of volatile products including SPF_3.

Summary and Conclusion

Unlike the reactions of F_2PS_2H with VCl_4 discussed herein and VCl_3,[3a] $OVCl_3$,[3a] O_2CrCl_2,[7] $MoCl_5$,[7] $MoCl_4$,[7] or $OMoCl_4$,[7] total replacement of chlorine was not achieved for $TiCl_4$, $NbCl_4$, $NbCl_5$, or $TaCl_5$, and the major products were complexes of the metals in their original valence states.

The major products in the reactions of HS_2PF_2 with $NbCl_5$ or $TaCl_5$ were the complexes $Cl_3M(S_2PF_2)_2$ (M = Nb, Ta), and in each case at least 2 mol of F_2PS_2H was consumed, and 2 mol of HCl or slightly more was evolved. The failure of the acid to reduce the oxidation states of the central metal atoms (except vanadium) illustrates the stability of the oxidation states 5+ (Nb, Ta) and 4+ (Ti) for these metals. The oxidation state 3+ is an important one for vanadium, and its resistance to oxidation to the 4+ state is greater than that of titanium. Thus the formation of the complex $V(S_2PF_2)_3$, with the highly favored six-coordination about vanadium, was most facile. The replacement of only one chlorine about titanium is surprising, when two chlorines are easily replaced by ligands such as acetylacetonate, but six-coordination about titanium could be satisfied by formation of a stable chlorine-bridged polynuclear complex which then does not suffer further replacement. It is of interest to note that, if the niobium and tantalum complexes are indeed nonionic, and the $F_2PS_2^-$ ligand is bidentate as suggested by the infrared and ^{19}F nmr spectra of the complexes, then these metals are in a seven-coordinate enviornment. Though uncommon, such an environment is known for these metals.[18,19]

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Linear Free Energy Relationships in the Mercury(II)-Catalyzed Aquation of Halopentaaquochromium(III) Complexes[1a]

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The kinetics of the mercury(II)-catalyzed aquations of the halopentaaquochromium(III) complexes have been determined at 0.500 *M* ionic strength. The general form of the rate law is $-d \ln [Cr(H_2O)_5X^{2+}]/dt = (k_0 + k_{-1}[H^+]^{-1})[Hg^{2+}]$. The values of k_0 (M^{-1} sec^{-1}) at 25.0° are $<2 \times 10^{-7}$, 0.0347, 288, and *ca.* 6×10^7 for X = F, Cl, Br, and I and of k_{-1} (sec^{-1}) are 0.0312 and 210 for X = Cl and Br. Values of k_0 were also determined for the reactions of $Cr(H_2O)_5I^{2+}$ with $HgCl^+$ and $HgCl_2$ to be 9.10×10^7 and 518 M^{-1} sec^{-1} at 25.0°. Activation parameters were determined for most of these reactions. A linear free energy relationship was established for the Hg^{2+}-catalyzed reactions and had a slope of 0.90 ± 0.02, indicating substantial breaking of the Cr–X bond and making of the Hg–X bond in the transition state, in agreement with results of chemical competition studies.

Introduction

The aquation of cobalt(III) complexes appears to proceed *via* formation of a five-coordinate intermediate with "good" leaving groups (generated by reactions such as $Co(NH_3)_5X^{2+} + Hg^{2+}$ (X = Cl, Br, I)[2] and $Co(NH_3)_5N_3^{2+} + HNO_2$[3]). With relatively "poor" leaving groups, the mechanism is still dissociative[4] but apparently does not involve the formation of an intermediate.[5] In the case of the unassisted aquation of acidopentaamminecobalt(III) complexes, Langford[6] has shown that the free energy of activation $\Delta G^{\ddagger}$ for the forward reaction is linearly related to the standard free energy change $\Delta G°$ for the overall reaction

$$Co(NH_3)_5X^{2+} + H_2O = Co(NH_3)_5OH_2^{3+} + X^- \quad (1)$$

A plot of the log of the first-order rate constants *vs.* the log of the corresponding equilibrium constants (X = F, H_2PO_4, Cl, Br, I, NO_3) is fully linear with a slope of 1.0.[6] For the analogous reactions of iridium(III) complexes, the slope of the linear free energy relationship (LFER) is 0.9.[7] Both studies suggest that the role of the departing ligand in the transition state

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(1) (a) Taken in part from the M.S. thesis of C. M. I., 1971. (b) National Science Foundation Trainee, 1969–1971.

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