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The Hexakis(fluorosulfato)stannate(IV) Ion

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Two synthetic routes to compounds containing the novel hexakis(fluorosulfato)stannate(IV) ion are discussed: $Sn(SO_3F)_4 + 2ClO_2SO_3F \rightarrow (ClO_2)_2[Sn(SO_3F)_6]$ and $M_2[SnCl_6] + 3S_2O_6F_2 \rightarrow M_2[Sn(SO_3F)_6] + 3Cl_2$, with M = K, Cs, or NO. The $[Sn(SO_3F_6)]^{2-}$ ion is characterized by ^{119}Sn Mossbauer, Raman, and infrared spectroscopy. Solutions in HSO_3F are studied by conductometry and ^{19}F nmr.

Introduction

Even though octahedrally coordinated hexahalometalates of the type $[MX_6]^{n-}$, with M = a main-group element of group IIIa, IVa, or Va, X = F, Cl, Br, or I and *n* ranging from 1 to 3, are very widely known, no examples where X is a fluorosulfate group have been reported. Here the largest number of SO_3F groups bonded to a central atom appears to be 4, observed in anions of the type $[Hal(SO_3F)_4]^-$[1,2] with Hal = Br or I, in neutral compounds such as $C(SO_3F)_4$[3] or $Sn(SO_3F)_4$[4] or in the mixed fluoro-fluorosulfato anion $[SbF_2(SO_3F)_4]^-$,[5] identified in solution only.

The assumptions that compounds with the anion $[M(SO_3F)_6]^{n-}$ may be synthesized and that tin is most likely a suitable central atom are based on the structural proposal for $Sn(SO_3F)_4$,[4] involving two monodentate and two bridging bidentate SO_3F groups, resulting in a polymer with hexacoordination around tin. This proposal is based on vibrational and ^{119}Sn Mossbauer spectra. The bidentate bridging configuration for the SO_3F group has subsequently been confirmed for the related compound $(CH_3)_2Sn(SO_3F)_2$[6] by X-ray diffraction.[7] Two feasible synthetic routes to compounds with the $[Sn(SO_3F)_6]^{2-}$ ion were contemplated: (a) the interaction of $Sn(SO_3F)_4$ as a fluorosulfate ion acceptor with a suitable fluorosulfate and (b) the complete substitution of chlorine in the hexachlorostannate ion, $[SnCl_6]^{2-}$, by fluorosulfate groups with peroxydisulfuryl difluoride,[8] $S_2O_6F_2$. This compound has been used previously in the synthesis of $Sn(SO_3F)_4$ from $SnCl_4$.[4]

It became interesting to see whether complexes with both univalent alkali metals and "heterocations"[9] such as K^+ and Cs^+ or ClO_2^+ and NO^+ could be obtained. Structural characterization should be possible using vibrational and ^{119}Sn Mossbauer spectroscopy. Solution studies in HSO_3F were of special interest, because the parent acid $H_2[Sn(SO_3F)_6]$ can be expected to be a strong acid, comparable perhaps to $H[SbF_2(SO_3F)_4]$[5] one of the main components in superacid media.[10]

Experimental Section

I. Chemicals. Potassium chloride, cesium chloride, and tin(IV) chloride were obtained from commercial sources in the highest degree of purity available. The hexachlorostannates K_2SnCl_6,[11] Cs_2SnCl_6,[11] and $(NO)_2SnCl_6$[12] and ClO_2SO_3F,[13] $Sn(SO_3F)_4$,[4] and $S_2O_6F_2$[14] were synthesized according to published methods. Technical grade fluorosulfuric acid (Allied Chemicals) was purified by double distillation as described earlier.[15] The purity was checked by specific conductance measurements.

II. Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. Silver chloride and silver bromide windows (all from Harshaw Chemicals) were used either with Nujol or without any mulling agent.

Raman spectra on the solid samples were obtained with a Cary 81 spectrometer, equipped with a Model 125 He-Ne gas laser (Spectra Physics Corp.). The 6328-Å wavelength line was used as exciting light. The samples were contained in 5-mm o.d. Pyrex tubes with flat bottoms.

The Mossbauer spectrometer has been described before in detail.[4] Measurements were made with the absorber either at 80 or at 298°K and the $Ba^{119m}SnO_3$ source at 298°K. All isomer shifts are reported relative to SnO_2 absorber at 80°K. The confidence limit for both isomer shifts and quadrupole splittings is judged to be ±0.03 mm/sec.

A HR100 nmr spectrometer from Varian Associates was used to obtain ^{19}F nmr spectra.

A Wayne-Kerr Universal Bridge No. B-221A was employed for the conductometric studies. The conductivity cells and the determination of cell constants have been described previously.[15] A Sargent Thermonitor, Model ST, with a circulating and heating unit was used in the constant-temperature bath, held at 25.00 ± 0.01°.

All manipulations of solid materials were carried out in a Vacuum Atmosphere Corp. "Dri-Lab" Model No. HE-43-2 filled with purified dry nitrogen and equipped with "Dri-Train" Model No. HE-93B.

III. Preparations. (a) $(ClO_2)_2[Sn(SO_3F)_6]$. Chloronium hexakis(fluorosulfato)stannate(IV) was prepared in a 100-ml erlenmeyer flask equipped with a Teflon stem stopcock (Kontes Glass Co.) and a Teflon-coated magnetic stirring bar by adding 0.849 g (5.02 mmol) of ClO_2SO_3F to 0.520 g (1.01 mmol) of $Sn(SO_3F)_4$ in a drybox at room temperature. To ensure complete reaction, about 10 ml of $S_2O_6F_2$ was added by vacuum distillation. The reaction mixture was heated to about 70° and stirred for several hours. A bright yellow solid, later identified as $(ClO_2)_2[Sn(SO_3F)_6]$, was isolated after $S_2O_6F_2$ and the excess ClO_2SO_3F were removed by vacuum distillation.

(b) $Cs_2[Sn(SO_3F)_6]$. An erlenmeyer reaction flask as described above was used. An approximately fivefold excess of $S_2O_6F_2$ was distilled *in vacuo* onto 0.731 g (1.22 mmol) of carefully dried Cs_2SnCl_6. The mixture was allowed to warm to room temperature where slow reaction under Cl_2 evolution occurred. The reactor was then heated at +50° for about 3 hr, and the mixture was stirred magnetically. When all gas evolution had ceased, the excess of $S_2O_6F_2$ was removed by vacuum distillation. A white solid (1.2114 g, 1.24 mmol) was obtained as a nonvolatile residue. Both $(NO)_2[Sn(SO_3F)_6]$ and $K_2[Sn(SO_3F)_6]$ were obtained in a similar manner. The reaction temperature was 50° for the former and 60° for the latter compound. A slightly impure sample of $K_2[Sn(SO_3F)_6]$ was obtained when K_2SnCl_6

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(1) M. Lustig and G. H. Cady, *Inorg. Chem.*, 1, 714 (1962).

(2) H. A. Carter, S. P. L. Jones, and F. Aubke, *Inorg. Chem.*, 9, 2485 (1970).

(3) D. D. Des Marteau, *Inorg. Chem.*, 7, 434 (1968).

(4) P. A. Yeats, B. L. Poh, B. F. E. Ford, J. R. Sams, and F. Aubke, *J. Chem. Soc. A*, 2188 (1970).

(5) R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, *Inorg. Chem.*, 4, 1641 (1965).

(6) P. A. Yeats, B. F. E. Ford, J. R. Sams, and F. Aubke, *Chem. Commun.*, 791 (1969).

(7) F. A. Allen, J. Lerbscher, and J. Trotter, *J. Chem. Soc. A*, 2507 (1971).

(8) F. B. Dudley and G. H. Cady, *J. Amer. Chem. Soc.*, 79, 513 (1957).

(9) A. A. Wolf, *Advan. Inorg. Chem. Radiochem.*, 9, 217 (1966).

(10) R. J. Gillespie, *Accounts Chem. Res.*, 1, 202 (1968).

(11) G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. 1, 2nd ed, Academic Press, New York, N. Y., 1963, p 731.

(12) H. Rheinboldt and R. Wasserfuhr, *Chem. Ber.*, 60, 732 (1927).

(13) H. A. Carter, A. M. Qureshi, and F. Aubke, *Chem. Commun.*, 1461 (1968).

(14) G. H. Cady and J. M. Shreeve, *Inorg. Syn.*, 7, 124 (1963).

(15) J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, 3, 1149 (1964).

was allowed to react with an excess of $BrOSO_2F$[16] at room temperature for about 15 min.

IV. Analysis. Elemental analysis was carried out by Alfred Bernhardt, 5251 Elbach uber Engelskirchen, West Germany.

(a) $(ClO_2)_2[Sn(SO_3F)_6]$. This is a bright yellow solid, thermally stable up to +130° where a dark red liquid forms with decomposition. It hydrolyzes very vigorously to a clear, chloride-free solution. *Anal.* Calcd for $(ClO_2)_2[Sn(SO_3F)_6]$: Sn, 14.00; S, 22.69; F, 13.44; Cl, 8.36. Found: Sn, 14.25; S, 22.84; F, 13.65; Cl, 8.11.

(b) $(NO)_2[Sn(SO_3F)_6]$. This is a white, hygroscopic solid, which decomposes at 94–97°. *Anal.* Calcd for $(NO)_2[Sn(SO_3F)_6]$: Sn, 15.35; S, 24.88; F, 14.75. Found: Sn, 15.57; S, 25.00; F, 15.02.

(c) $K_2[Sn(SO_3F)_6]$. This is a white, hygroscopic solid, which decomposes at 235–238°. *Anal.* Calcd for $K_2[Sn(SO_3F)_6]$: Sn, 15.00; S, 24.31; F, 14.41. Found: Sn, 14.84; S, 24.58; F, 14.20.

(d) $Cs_2[Sn(SO_3F)_6]$. This is a white, hygroscopic solid, which decomposes at 249–253°. *Anal.* Calcd for $Cs_2[Sn(SO_3F)_6]$: Sn, 12.13; S, 19.65; F, 11.65. Found: Sn, 11.80; S, 19.60; F, 11.54.

Results and Discussion

I. Synthesis. Salts containing the $[Sn(SO_3F)_6]^{2-}$ ion are obtained in a simple manner, either by complex formation

$$2ClO_2SO_3F + Sn(SO_3F)_4 \xrightarrow[S_2O_6F_2]{+70°,\ 3\ hr} (ClO_2)_2[Sn(SO_3F)_6]$$

or by ligand substitution

$$M^I{}_2[SnCl_6] + 3S_2O_6F_2 \xrightarrow{50-60°,\ 4\ hr} M^I{}_2[Sn(SO_3F)_6] + 3Cl_2$$

with $M^I = NO^+, K^+$, or Cs^+.

All compounds show high thermal stability, in particular the potassium and the cesium salts. This suggests that other salts, *e.g.*, $Rb_2[Sn(SO_3F)_6]$ or $Na_2[Sn(SO_3F)_6]$, may well exist, but no attempts at their synthesis were made.

A third synthetic route may be seen in the heterocation substitution[9] of ClO_2^+ by NO^+ or NO_2^+. The interaction of $(ClO_2)_2[Sn(SO_3F)_6]$ with an excess of NO or NO_2 at room temperature resulted in the expected formation of $ClONO_2$[17] identified by its infrared spectrum[18] but the solid residue still contained small amounts of ClO_2^+ thus indicating incomplete substitution.

All hexakis(fluorosulfato)stannates(IV) are very soluble in HSO_3F, quite in contrast to the polymeric $Sn(SO_3F)_4$[4] which is virtually insoluble even when the SO_3F^- concentration of HSO_3F is enhanced by addition of KSO_3F. This fact may serve as preliminary evidence that the obtained products are not merely mixtures of M^ISO_3F and $Sn(SO_3F)_4$.

II. ^{119}Sn Mossbauer Spectra. The observed ^{119}Sn Mossbauer data for the hexakis(fluorosulfato)stannates(IV) are listed in Table I, together with literature data for a number of related compounds. All new compounds are found to give single-line spectra with identical isomer shift values within the limits of accuracy. The absence of any resolvable quadrupole splitting indicates a spherical charge distribution around tin, consistent with an octahedral environment for the central atom. The slightly wider Γ values for the NO^+ and the ClO_2^+ compounds may indicate some unresolved splitting for these complexes and hence a distorted octahedral structure.

In general, the similarity between fluoro[19] and fluorosulfato compounds is apparent, in particular the transition from well-resolved quadrupole splittings for SnF_4 and $Sn(SO_3F)_4$ to the single-line spectra found generally for the anionic complexes. However, some interesting differences between both groups deserve attention.

Table I. ^{119}Sn Mossbauer Spectra at 80°K

Compound	Isomer shift,[a] δ, mm/sec	Quadrupole splitting, Δ, mm/sec	Line width,[f] Γ, mm/sec	Remarks
$K_2[Sn(SO_3F)_6]$	−0.260		1.14	No RT[b] spectrum
$Cs_2[Sn(SO_3F)_6]$	−0.25		1.11	
$(NO)_2[Sn(SO_3F)_6]$	−0.28		1.41	
$(ClO_2)_2[Sn(SO_3F)_6]$	−0.30		1.28	
$Sn(SO_3F)_4$[c]	−0.27	1.34	1.05, 1.32	R[d] = 0.42
SnF_4[c]	−0.26	1.80		$R = 0.73$
$K_2[SnF_6]$[e]	−0.43		1.59	$R = 0.61$
$(ClO_2)_2[SnF_6]$[e]	−0.40	1.01	1.46, 1.46	$R = 0.71$
$K_2[SnCl_6]$[e]	+0.48		1.35	$R = 0.38$

[a] Relative to SnO_2. [b] RT effect = Mossbauer effect at room temperature. [c] See ref 4. [d] $R = \epsilon_{298}/\epsilon_{80}$ with ϵ_T = magnitude of the Mossbauer effect at T°K. [e] See ref 19. [f] Line width at half peak height.

Even though SnF_4 and $Sn(SO_3F)_4$ have identical isomer shift values, the hexafluorostannates(IV) exhibit slightly lower δ values by about 0.10–0.15 mm/sec than the corresponding fluorosulfate complexes. This indicates a slightly less positive effective nuclear charge on tin for the latter group of compounds, probably caused by a lower electronegativity of the SO_3F group. To derive numerical electronegativity values for this group seems not too meaningful in the light of recent discussions on related systems.[20–23]

The absence of any observable quadrupole splitting for $(ClO_2)_2[Sn(SO_3F)_6]$ is in contrast to observations for $(ClO_2)_2[SnF_6]$, where a Δ value of 1.01 mm/sec was observed.[19] Since in the latter compound the apparent charge asymmetry is caused by appreciable cation–anion interaction—also evident from the vibrational spectrum for $(ClO_2)_2[SnF_6]$—it must be concluded that a similar interaction is either absent for $(ClO_2)_2[Sn(SO_3F)_6]$ or effectively buffered by the SO_3F groups and not relayed to the tin atom.

Finally, whereas all hexafluorostannates(IV) give well-resolved Mossbauer spectra even at room temperature,[19] the fluorosulfato derivatives did not seem to show the same behavior. No resolvable spectrum could be obtained for $K_2[Sn(SO_3F)_6]$, and $(ClO_2)_2[Sn(SO_3F)_6]$ was found to interact with the Mylar windows at ambient temperature. The difference here may be caused by differences in the Debye temperature for both types of solids.

III. Vibrational Spectra. Both Raman and infrared spectra were recorded for all four compounds, the latter ranging down to ~400 cm^{-1} only, because only silver halide windows were found to be resistant. As expected, absorption bands due to the $[Sn(SO_3F)_6]^{2-}$ ion are found in rather identical regions for all four compounds. The discussion will therefore center around $(ClO_2)_2[Sn(SO_3F)_6]$ and $K_2[Sn(SO_3F)_6]$, for which the observed frequencies are listed in Table II, together with estimated intensities and a rather approximate assignment.

Even though relatively good agreement with previous work[2] on solid compounds with monodentate OSO_2F groups is noted, *e.g.*, with $[Hal(SO_3F)_4]^-$, and utilized in the assignment, extensive vibrational coupling and solid-state splitting result in complex absorption bands, in particular in the SO and the SF stretching range. This is more apparent from the Raman spectra than the rather broad and only partly resolved

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(16) F. Aubke and R. J. Gillespie, *Inorg. Chem.*, 7, 599 (1968).

(17) H. Martin, *Angew. Chem.*, 70, 97 (1958).

(18) R. H. Miller, D. L. Bernitt, and I. C. Hisatsune, *Spectrochim. Acta, Sect. A*, 23, 223 (1967).

(19) H. A. Carter, A. M. Qureshi, and F. Aubke, *Can. J. Chem.*, 48, 2853 (1970), and references therein.

(20) R. H. Herber and H. S. Cheng, *Inorg. Chem.*, 8, 2145 (1969).

(21) H. S. Cheng and R. H. Herber, *Inorg. Chem.*, 9, 1686 (1970).

(22) C. A. Clausen and M. L. Good, *Inorg. Chem.*, 9, 817 (1970).

(23) J. E. Huheey and J. C. Watts, *Inorg. Chem.*, 10, 1553 (1971).

Table II. Vibrational Spectra of $(ClO_2)_2[Sn(SO_3F)_6]$ and $K_2[Sn(SO_3F)_6]$

$(ClO_2)_2[Sn(SO_3F)_6]$		$K_2[Sn(SO_3F)_6]$		
Raman $\Delta\nu$, cm^{-1}	Ir ν, cm^{-1}	Raman $\Delta\nu$, cm^{-1}	Ir ν, cm^{-1}	Proposed assignment
1412 w	1420 m, sh	1407 m	1380 s, b	SO_2 asym str
1386 s	1378 s	1390 m		
1308 m	1303 w			$\nu_3(ClO_2^+)$, asym ClO_2 str
1295 w	1290 m			
1265 ms		1278 ms		?
1206 s	1215 s, b	1228 m	1220 b, sh	SO_2 sym str
1092 m	1180 m, sh	1208 w	1190 s, b	
1062 vw		1096 s		
1030 s	1025 s			$\nu_1(ClO_2^+)$, sym ClO_2 str
	1008	1002 m	990 s, b	O-SO_2F str
990 sh	995 m, sh			
		859 m	820 s, sh	ν(SF)
842 m	830 s, b	836 m		
820 m	810 s, sh	823 m	810 s, b	
624 s	628 m	625 s	620 s	Sn-O-S bend
582 m	576 m	582	571	SO_2 bend
555 m	550 m	560 m	550 s	SO_2 rock
526 m	519 m			$\nu_3ClO_2^+$, ClO_2 bend
429	430 m	435 m	430 m	SF wagging
399 w	402 w	416 m		S-O wagging
348 m		360 m		SnO str?
264 w		266 w		SO_2F torsion

infrared spectra. So, *e.g.*, ν(SF) for $K_2[Sn(SO_3F)_6]$ is split into three components. Nevertheless the broad infrared bands at ~1400, ~1200, ~1000, and ~820 cm^{-1} are in the expected range for solid fluorosulfato complexes[2,24] with monodentate covalent SO_3F groups. The additional splitting is not unexpected.

As can be seen from Table II, the absorption bands due to the ClO_2^+ ion are in a region similar to those observed previously.[19,25] Again, ν_3 is split into two components presumably caused by ^{35}Cl and ^{37}Cl isotopes. For $(NO)_2[Sn(SO_3F)_6]$, ν(NO) is found at 2334 cm^{-1}, as compared with 2207 cm^{-1} for $(NO)_2[SnCl_6]$[19,26] or with 2325 cm^{-1} for $(NO)_2[SnF_6]$.[19] The findings for both heterocation complexes are thus consistent with an ionic formulation.

Finally, the absence of any absorption at ~750 cm^{-1}, characteristic for ν(SF) in ionic SO_3F^- groups,[27,28] is good evidence for the $[Sn(SO_3F_6]^{2-}$ ion rather than a mixture of, *e.g.*, KSO_3F and $Sn(SO_3F)_4$.

IV. Solution Studies in HSO_3F. The solutions of $K_2[Sn(SO_3F)_6]$ and $(ClO_2)_2[Sn(SO_3F)_6]$ in HSO_3F are found to be moderately strongly basic as confirmed by subsequent titration with the standard base KSO_3F.[29] The calculated γ values[15] for concentrations up to ~6.0×10^{-2} mol/kg are listed in Table III. A plot of concentration *vs.* specific conductance is shown in Figure 1.

Clear solutions were obtained even at the higher concentration ranges required for ^{19}F nmr studies. This excludes the possibility that $Sn(SO_3F)_4$, which is insoluble in HSO_3F, may be formed. For $K_2Sn(SO_3F)_6$ only a single ^{19}F nmr line could be found at −41.37 ppm downfield from $CFCl_3$ used as external standard. In addition the signal for HSO_3F is found at −40.76 ppm, virtually unchanged from the position in the neat solvent. This finding excludes any appreciable SO_3F exchange between solute and solvent at room temperature.

Table III. Electrical Conductance of $K_2[Sn(SO_3F)_6]$ and $(ClO_2)_2[Sn(SO_3F)_6]$ in HSO_3F at 25.00° (γ Values)

Specific conductance $\times 10^4$, ohm^{-1} cm^{-1}	γ values	
	$K_2[Sn(SO_3F)_6]$[a]	$(ClO_2)_2[Sn(SO_3F)_6]$[b]
10	0.73	0.59
15	0.63	0.55
20	0.58	0.51
25	0.55	0.48
30	0.52	0.45
35	0.49	0.44

[a] Experimental concentration range: 1.6×10^{-4} to 6.3×10^{-2} mol kg^{-1}. [b] Experimental concentration range: 3.0×10^{-5} to 3.5×10^{-2} mol kg^{-1}.

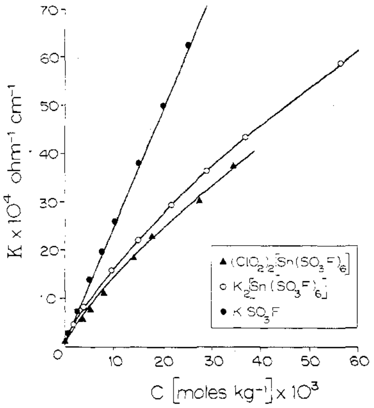

Figure 1. Conductivities of $K_2[Sn(SO_3F)_6]$ and $(ClO_2)_2[Sn(SO_3F)_6]$ at 25°.

As seen in Figure 1, the solutions of $(ClO_2)_2[Sn(SO_3F)_6]$ are slightly less conducting than those of $K_2[Sn(SO_3F)_6]$. The identical order had been observed previously for solutions of KSO_3F and ClO_2SO_3F[13] in HSO_3F and had been attributed to differences in the mobilities of the solvated cations. The formation of the solvated ClO_2^+ cation is evidenced by the yellow to orange color of the solutions of $(ClO_2)_2[Sn(SO_3F)_6]$.

The nmr evidence points to a rather simple mode of ionization without appreciable condensation, polymerization, or dissociation. Of the three possible modes

$$X_2[Sn(SO_3F)_6] \xrightarrow{HSO_3F} 2X^+(solv) + [Sn(SO_3F)_6]^{2-}(solv) \quad (1)$$

$$X_2[Sn(SO_3F)_6] + HSO_3F \overset{HSO_3F}{\rightleftarrows} 2X^+(solv) + H[Sn(SO_3F)_6]^-(solv) + SO_3F^-(solv) \quad (2)$$

$$X_2[Sn(SO_3F)_6] + 2HSO_3F \rightleftarrows 2X^+(solv) + H_2[Sn(SO_3F)_6](solv) + 2SO_3F^-(solv) \quad (3)$$

with X = K or ClO_2, the expected γ values would be 0, 1, or 2, respectively. The observed value of ~0.5 indicates an equilibrium with $[Sn(SO_3F)_6]^{2-}$ and $H[Sn(SO_3F)_6]^-$ as the most dominant tin species. The fact that both are indistinguishable in the nmr spectrum may be attributed to fast proton exchange between both ions.

It appears that the neutral acid $H_2[Sn(SO_3F)_6]$ behaves as a good proton donor in HSO_3F. This is not surprising since $H[SbF_2(SO_3F)_4]$[10] is also a rather strong acid or proton donor in this solvent system.

It must be concluded that the hexakis(fluorosulfato)stannate(IV) moiety can also exist in solutions of strong protonic acid without appreciable alteration.

Registry No. $(ClO_2)_2[Sn(SO_3F)_6]$, 37477-88-6; $(NO)_2[Sn(SO_3F)_6]$, 37534-26-2; $K_2[Sn(SO_3F)_6]$, 37477-89-7; Cs_2-

(24) A. M. Qureshi and F. Aubke, *Inorg. Chem.*, 10, 1116 (1971).

(25) K. O. Christie, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, 8, 2489 (1969).

(26) D. W. A. Sharp and J. Thorley, *J. Chem. Soc.*, 3557 (1963).

(27) A. Ruoff, J. B. Milne, G. Kaufmann, and M. Leroy, *Z. Anorg. Allg. Chem.*, 372, 119 (1970).

(28) A. M. Qureshi, H. A. Carter, and F. Aubke, *Can. J. Chem.*, 49, 35 (1971).

$[Sn(SO_3F)_6]$, 37477-90-0; $Sn(SO_3F)_4$, 28646-46-0; ClO_2SO_3F, 24114-30-5; $S_2O_6F_2$, 13709-32-5; $K_2[SnCl_6]$, 16923-42-5; $Cs_2[SnCl_6]$, 17362-93-5; $(NO)_2[SnCl_6]$, 30406-43-0.

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Contribution from the Department of Chemistry, Georgetown University, Washington, D. C. 20007

Heteropoly 12-Metallophosphates Containing Tungsten and Vanadium. Preparation, Voltammetry, and Properties of Mono-, Di-, Tetra- and Hexavanado Complexes[1,2]

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Alkali salts of the anions $PVW_{11}O_{40}{}^{4-}$ (I), $PV_2W_{10}O_{40}{}^{5-}$ (II), $HPV_4W_8O_{40}{}^{6-}$ (III), and $H_3PV_6W_6O_{40}{}^{6-}$ (IV) have been prepared and analyzed. Stationary-electrode voltammetry using wax-impregnated carbon and pyrolytic graphite electrodes has been used to characterize these complexes in solution. The anions I–IV undergo one-, two-, four-, and six-electron reductions, respectively, at potentials between +0.58 and −0.04 V *vs.* sce. The voltammograms are sufficiently characteristic to allow identification of these complexes in mixtures and to trace their reactions. The kinetics of conversion of I into II at pH 3.9 and 4.9 have been followed. The reaction is second order in I and is consistent with a hydrolytic disproportionation, a process which parallels reactions of heteropoly blues. Preparation of vanadium-containing heteropoly anions by the "etherate" method has been shown to give variable results.

Introduction

The existence of heteropoly anions containing simultaneously atoms of tungsten(VI), molybdenum(VI), and/or vanadium(V) has long been considered plausible. In particular, many examples of heteropoly complexes in which the atomic ratio of central atom P(As, Si, Ge):W(Mo) + V = 1:12 have been reported.[5-13] Following the determination of the structure of $PW_{12}O_{40}{}^{3-}$ in 1933,[14] it has tacitly been assumed that the materials described in ref 5–13 contained anions with the same ("Keggin") structure. While this is doubtless the case, the authenticity and chemical individuality of some of the reported "mixed heteropoly anions" remains dubious. In only a few cases have well-analyzed recrystallizable materials been described, and many conclusions about the existence of certain complexes have been based upon solution measurements, which are open to other interpretations. In the P-W-V and P-Mo-V systems, careful work by independent groups[11-13] has identified the complexes $PV_xW_{12-x}O_{40}{}^{n-}$ ($x = 1, 2, 6, 10$) and $PV_xMo_{12-x}O_{40}{}^{n-}$ ($x = 1, 2, 3, 6, 10$). Some earlier work[10] on the other hand only indicated the existence of complexes with $x = 2$.

The present work, originally undertaken in connection with our studies of heteropoly blues,[15] has resulted in the isolation and confirmation of the complex, $PV_4W_8O_{40}{}^{7-}$. This complex was specifically excluded in the scheme of P-V-W heteropoly anions proposed by Courtin,[13] although others have described materials that may have contained such an anion.[16,17] This paper also reports the first successful voltammetric studies of vanadium-containing polyanions; other investigators have used the dropping mercury electrode (dme) with consequent chemical reduction of vanadium(V) by mercury.

Experimental Section

Preparation of Complexes. The preparation of alkali salts of $Co^{II}W_{12}O_{40}{}^{6-}$, $SiW_{12}O_{40}{}^{4-}$, $PW_{12}O_{40}{}^{3-}$, and $P_2W_{18}O_{62}{}^{6-}$ has been described before.[18,19]

Ammonium (Potassium) 8-Tungsto-4-vanadophosphate. A solu-

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[5] Various Ph.D. dissertations of students of C. Friedheim, University of Berne, 1900–1909; "Gmelins Handbuch," System-Nr. 53, Molybdan, Verlag Chemie, Berlin, 1935, p 383.

[6] C. Friedheim and W. H. Henderson, *Ber.*, 35, 3242 (1902).

[7] H. Wu, *J. Biol. Chem.*, 43, 189 (1920).

[8] G. Canneri, *Gazz. Chim. Ital.*, 56, 642, 871 (1926).

[9] R. E. Kitson and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, 16, 379 (1944).

[10] A. I. Kokorin, M. B. Bardin, and N. A. Polotebnova, *Uch. Zap., Kishinev. Gos. Univ.*, 7, 59 (1953); *Chem. Abstr.*, 51, 930*b* (1953); A. I. Kokorin, *Zh. Obshch. Khim.*, 24, 966 (1954); A. I. Kokorin and N. A. Polotebnova, *ibid.*, 26, 3 (1956); 27, 304, 549 (1957); Z. F. Shakhova, G. N. Tishchenko, and R. I. Motorkina, *ibid.*, 27, 1118 (1957); R. K. Motorkina, *Zh. Neorg. Khim.*, 2, 92 (1957); A. I. Kokorin, *Nauch. Dokl. Vyssh. Shk., Khim. Khim. Tekhnol.*, 3, 775 (1958); *Tr. Kom. Anal. Khim., Akad. Nauk SSSR*, 8, 88 (1958).

[11] P. Courtin, F. Chauveau, and P. Souchay, *C. R. Acad. Sci.*, 258, 1247 (1964); P. Courtin and F. Chauveau, *Bull. Soc. Chim. Fr.*, 2461 (1967); P. Souchay, F. Chauveau, and P. Courtin, *ibid.*, 2384 (1968).

[12] G. A. Tsigdinos and C. J. Hallada, *Inorg. Chem.*, 7, 437 (1968); C. J. Hallada, G. A. Tsigdinos, and B. S. Hudson, *J. Phys. Chem.*, 72, 4304 (1968).

[13] P. Courtin, *Bull. Soc. Chim. Fr.*, 4799 (1968); *Rev. Chim. Miner.*, 8, 75, 221 (1971).

[14] J. F. Keggin, *Proc. Roy. Soc., Ser. A*, 144, 75 (1934).

[15] See, for example, G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, 9, 662 (1970).

[16] It is very likely that the compound formulated as $13(NH_4)_2O\cdot 2P_2O_5\cdot 8V_2O_5\cdot 34WO_3\cdot 86H_2O$ by A. Rogers, *J. Amer. Chem. Soc.*, 25, 299 (1903), is an acid salt of $PV_4W_8O_{40}{}^{7-}$. See also L. C. W. Baker, B. Loev, and T. P. McCutcheon, *J. Amer. Chem. Soc.*, 72, 2374 (1950).

[17] N. A. Polotebnova and Y. L. Neimark, *Russ. J. Inorg. Chem.*, 11, 751 (1966).

[18] M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, 5, 1249 (1966).

[19] M. T. Pope and E. Papaconstantinou, *Inorg. Chem.*, 6, 1147 (1967).