27. *Protactinium*(V) *Sulphates and Selenates.*

By K. W. Bagnall, D. Brown, and P. J. Jones.

A protactinium(V) acid trisulphato-complex, $H_3PaO(SO_4)_3$, and the corresponding triselenato-complex, $H_3PaO(SeO_4)_3$, have been prepared. *X*-Ray diffraction and infrared data are reported for these compounds. The sulphato-complex decomposes to $HPaO(SO_4)_2$ at 375°. The preparation of potassium sulphatoprotactinates(V) from aqueous solution has also been attempted.

AQUEOUS sulphuric acid solutions of protactinium(V) are relatively stable to hydrolysis,[1] [2] which suggests the formation of sulphato-complexes. Ion-exchange and solvent-extraction studies [2] indicate the existence of species of charge -1 in equilibrium with cationic species in solutions less than 0·5M in sulphuric acid, while at higher acidities further complex-formation produces species of charge -3. An incompletely characterised potassium sulphatoprotactinate(V) has been reported [3,4] as being precipitated on addition of aqueous potassium sulphate solutions to protactinium(V) in dilute sulphuric acid; and a compound claimed to be protactinium pentasulphate, $Pa_2(SO_4)_5$, is said [5] to crystallise from fuming sulphuric acid, and has been used to eliminate niobium, which is relatively soluble in this medium. The pentasulphate, however, was formulated on the basis of protactinium analyses only, and it appeared worth while to investigate further the behaviour of protactinium(V) in sulphuric acid. Since no published information is available on the properties of protactinium(V) in selenic acid the formation of selenato-complexes has also been investigated.

The white, moisture-sensitive hydrogen oxotrisulphatoprotactinate(V), $H_3PaO(SO_4)_3$ crystallises readily in almost quantitative yield when a solution of protactinium(V) in a mixture of hydrofluoric and sulphuric acids is evaporated until all fluoride has been eliminated. The use of hydrofluoric acid is necessary to ensure complete dissolution of the starting material, protactinium pentoxide, and, in addition, enables one to use more concentrated, stable solutions of protactinium(V) (~200 mg./ml.) than can be obtained by dissolving the freshly precipitated hydroxide in dilute sulphuric acid. The analogous selenato-complex, $H_3PaO(SeO_4)_3$, is obtained in a similar fashion from hydrofluoric–selenic acid mixtures. The solubility of these compounds in their parent acids is less than 1 mg./ml. and they are essentially insoluble in anhydrous nitrobenzene, benzene, ethyl acetate, ether, di-isobutyl ketone, nitromethane, and methyl cyanide. The sulphato-complex dissolves readily in dilute sulphuric acid and is easily destroyed by 6M-hydrochloric acid or aqueous ammonia, whereas the selenate, which dissolves readily in dilute sulphuric acid, is fairly stable to boiling 6M-hydrochloric acid and is incompletely hydrolysed by concentrated aqueous ammonia. Both complexes dissolve in dilute hydrofluoric acid, presumably with the formation of stable fluoro-complexes.

In a preliminary study, these complexes were freed from excess of sulphuric or selenic acid by being heated in a vacuum at 150—200° for several hours; this resulted in slightly high values for the metal contents and a ratio of Pa : anion of less than 1 : 3 (between 1 : 2·8 and 1 : 2·92), indicating probable thermal decomposition. However, it was also possible that the complexes were not oxoprotactinates(V) but the compounds $HPa(SO_4)_3$ and $HPa(SeO_4)_3$, severally, for the theoretical analyses are little different [*e.g.*, $H_3PaO(SO_4)_3$ requires Pa 42·9%; SO_4^{2-} 53·5%; and $HPa(SO_4)_3$ requires Pa 44·4%; SO_4^{2-} 55·4%] and it was possible that the compounds might not have been completely decomposed by aqueous ammonia during the analytical procedure. The preparative procedure was therefore

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[1] Brown and Maddock, *Quart. Rev.*, 1963, **17**, 289.

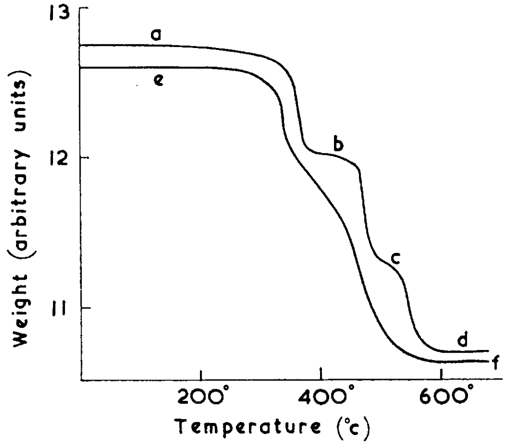
[2] Brown, Sato, Smith, and Wilkins, *J. Inorg. Nuclear Chem.*, 1961, **23**, 91.

[3] Maddock, unpublished results.

[4] Haissinsky and Bouissières, *Bull. Soc. chim. France*, 1957, **18**, 557.

[5] Kirby, Mound Lab., personal communication.

modified (see Experimental section) and attempts were made to differentiate between these possibilities, and particularly to preclude analytical errors due to the presence of traces of the organic solvent used latterly to remove the sulphuric or selenic acid. *X*-Ray powder photography did not help to differentiate the possibilities, since no analogous sulphates in selenates exist. Similarly, owing to the strong, very broad sulphate and selenate bands or the infrared spectra, the presence of a band due to a Pa=O stretching vibration, expected between 900 and 1000 cm.$^{-1}$, was uncertain. Thermogravimetric analyses (shown in the Figure) indicated the existence of reasonably stable lower sulphato-complexes but no corresponding selenates were formed. The observed weight losses could be interpreted for either possible starting sulphato-complex, with reasonable agreement between observed and calculated values (Table 1) for the decomposition (1) and (2):



Thermal degradation of (a—d) $H_3PaO(SO_4)_3$ and (e, f) $H_3PaO(SeO_4)_3$.

(a) $H_3Pa(SO_4)_3$.
(b) $HPaO(SO_4)_2$.
(c) $HPaO_2(SO_4)$·
(d) Pa_2O_5.
(e) $H_3PaO(SeO_4)_3$.
(f) Pa_2O_5.

$$(1)\ 2H_3PaO(SO_4)_3 \xrightarrow[-2H_2SO_4]{A} 2HPaO(SO_4)_2 \xrightarrow[-2SO_3]{B} 2HPaO_2SO_4 \xrightarrow[-H_2SO_4]{C} Pa_2O_5$$

$$(2)\ 2HPa(SO_4)_3 \xrightarrow[-H_2SO_4,\ -SO_3]{D} Pa_2O(SO_4)_4 \xrightarrow[-2SO_3]{E} Pa_2O_3(SO_4)_2 \xrightarrow[-2SO_3]{F} Pa_2O_5$$

but process A requires the elimination of twice as much sulphuric acid as does process D.

Accordingly, a sample of the trisulphatoprotactinate(V) was decomposed under a vacuum at 375—400° and at 750° in vessels that had been previously heated to 500° to ensure the absence of adsorbed water. Titration of the eliminated sulphuric acid, which was collected in a cooled part of each vessel, showed that the complex was in fact the oxotrisulphatoprotactinate(V) as suggested by the analytical figures, since heating at 375—400° to prepare the first decomposition product produced 1 mole of sulphuric acid per mole of complex and total decomposition at 750° yielded 1·4 moles of acid per mole of complex. It was possible to isolate the first decomposition product, $HPaO(SO_4)_2$, in an essentially pure state, the composition ranging from $HPaO(SO_4)_{1\cdot9}$ to $HPaO(SO_4)_{2\cdot1}$ depending on the period of heating at 375—400°, but no attempt was made to characterise the second product indicated by the thermal analysis (see Figure) owing to the short temperature range over which it appeared to be stable.

TABLE 1.

Weight losses (%) on thermal decomposition of protactinium salt. [A—F refer to the steps in reactions (1) and (2).]

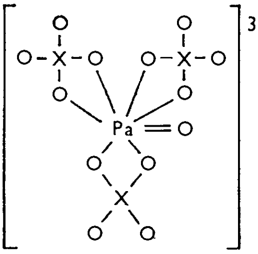
	A	D	B	E	C	F
Theor.	18·2	17·1	33·1	32·5	49·6	47·9
Obsd.	17·9		35·1		49·1	

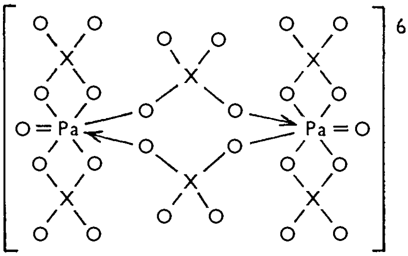
The infrared spectra of the complexes suggest that both monodentate and bidentate sulphate and selenate groups may be present since ν_3 and ν_4 are each split into 3 bands. Whereas the free $[SO_4]^{2-}$ ion (point group T_d) has only two infrared active vibrations, ν_3 and ν_4, the symmetry is lowered on co-ordination with resulting activation of the previously inactive infrared vibrations ν_1 and ν_2 and splitting of the degenerate vibrations ν_3 and ν_4. Thus the number of infrared-active vibrations [6] for a monodenate sulphate group is six (point group C_{3v}), and for a bidentate group is eight (point group C_{2v}). Table 2 lists the vibrations observed for the oxotrisulphatoprotactinate(V) and the triselenato-complex. The fact that ν_4 for the sulphato-complex appears only as two bands may be due to a combination of the relative numbers of monodentate and bidentate sulphate groups and differences in their intensities. This spectrum shows a broad intense absorption between 1250 and 900 cm.$^{-1}$ with poor peak resolution and no Pa=O stretching vibration, expected between 1000 and 900 cm.$^{-1}$, can be identified with certainty; it is probable that it appears as a relatively weak absorption masked by the sulphate bands. Similarly, the selenato-complex showed intense absorption between 950 and 725 cm.$^{-1}$ with a well-defined peak at 914 cm.$^{-1}$ and others at 860 and 801 cm.$^{-1}$. A much weaker band at 1136 cm.$^{-1}$ may be an overtone, since a similar band has been observed in the spectra of other selenates.[7] The decomposition product $HPaO(SO_4)_2$ shows much the same spectrum as does $H_3PaO(SO_4)_3$ but with poorer peak resolution; it is interesting that no new bands are observed below 900 cm.$^{-1}$ where the stretching vibration of the oxygen-bridged group Pa–O–Pa would be expected. This confirms the view that the decomposition product is $HPaO(SO_4)_2$ and not $Pa_2O(SO_4)_4$, which would be expected from the compound $HPa(SO_4)_3$. Since bidentate and bridging sulphate groups cannot be distinguished by infrared spectroscopy because they have the same point group, it is not possible on the available evidence

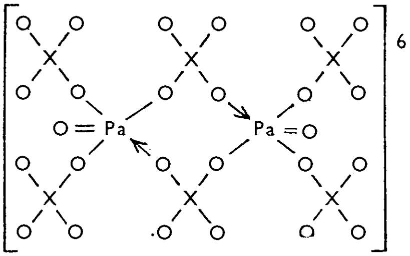
TABLE 2.

Infrared vibrational frequencies (cm.$^{-1}$) of oxotrisulphato- and oxotriselenato-protactinate(V).

	ν_1	ν_2	ν_3	ν_4		ν_1	ν_2	ν_3	ν_4
$H_3PaO(SO_4)_3$	975s	436w	1017s	616m	$H_3PaO(SeO_4)_3$	—	325w	914s	450w
			1114s	598m				860s	419m
			1179s	—				801s	395m


(I)


(II)

(III)


X = S or Se

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[6] Nakamoto, Fujita, Tanaka, and Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.

[7] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

to decide whether the trisulphato- and triselenato-complexes are monomeric and 8-co-ordinate (I) with three bidentate groups, dimeric and 8-co-ordinate (II) with bidentate and bridging groups, or dimeric and 6-co-ordinate (III) with monodentate and bridging groups.

X-Ray diffraction powder photographs of the trisulphato- and triselenato-complexes show them to be hexagonal, with 2 moles in the unit cell and calculated densities of 4·275 and 4·830 g./cm.^{3}, respectively. For the sulphate $a = 9{\cdot}439 \pm 0{\cdot}005$ Å, $c = 5{\cdot}506 \pm 0{\cdot}005$ Å, and for the selenate $a = 9{\cdot}743 \pm 0{\cdot}005$ Å, $c = 5{\cdot}679 \pm 0{\cdot}005$ Å: the space group is C_6^6-$P6_3$, C_{6h}^2-$P6_3m$, or D_6^6-P$6_3$22. Observed and calculated values of $\sin^2\theta$ for the reflections are listed (Table 3) with visually estimated intensities. The compound $HPaO(SO_4)_2$ was *X*-ray-amorphous.

Freshly precipitated protactinium(V) hydroxide is fairly soluble in 3M-sulphuric acid (~15 mg./ml.) and, while no precipitation is observed on the addition of potassium hydrogen sulphate to such solutions, it is almost quantitative from 1·5M-sulphuric acid in the presence of a large excess of the potassium salt. However, analytical figures for the product were inconsistent; after repeated washing with dilute sulphuric acid to remove the excess of potassium hydrogen sulphate and finally with anhydrous dioxan to remove the sulphuric acid, ratios of $K^+ : Pa : SO_4^{2}$ between 0·66 : 1 : 1·35 and 0·85 : 1 : 1·5 were obtained. Since the final product was probably a mixture, this system was not investigated further.

It is interesting that the protactinium(V) sulphates show no resemblance to those of niobium(V) prepared in a similar system,[8] namely, $Nb_2O_4SO_4$, $Nb_2O_3(SO_4)_2$, and $Nb_2O_2(SO_4)_3$. Previously,[9] $Nb_2O(SO_4)_4$ had been prepared by the action of sulphur trioxide on niobium pentachloride dissolved in sulphuryl chloride; rather surprisingly, it was stated that under the same conditions tantalum pentasulphate, $Ta_2(SO_4)_5$, was obtained. Recently,[10] however, it has been suggested that these niobium and tantalum compounds should be formulated as polysulphates, $(NbO_2)_2S_4O_{13}$ and $(TaO_2)_2S_5O_{16}$, respectively.

TABLE 3.

X-Ray diffraction results.

$H_3PaO(SO_4)_3$ sin$_2$ θ obs.	$H_3PaO(SO_4)_3$ sin$_2$ θ calc.	$H_3PaO(SeO_4)_3$ sin$_2$ θ obs.	$H_3PaO(SeO_4)_3$ sin$_2$ θ calc.	*h,k,l*	*I*
0·0089	0·0089	0·0083	0·0083	1,0,0	S
0·0266	0·0266	0·0249	0·0250	1,1,0	S−
0·0284	0·0284	0·0266	0·0267	1,0,1	S
0·0355	0·0355	0·0332	0·0333	2,0,0	M+
0·0462	0·0462	0·0433	0·0434	1,1,1	S−
0·0551	0·0551	0·0517	0·0517	2,0,1	S+
0·0621	0·0621	0·0584	0·0583	2,1,0	M+
0·0783	0·0783	0·0736	0·0736	0,0,2	S−
0·0799	0·0799	0·0750	0·0750	3,0,0	S−
0·0818	0·0817	0·0767	0·0767	2,1,1	S
0·0871	0·0871	0·0819	0·0819	1,0,2	W+
0·1049	0·1049	0·0987	0·0986	1,1,2	M
0·1067	0·1066	0·0999	0·1000	2,2,0	M
0·1138	0·1138	0·1071	0·1069	2,0,2	M+
0·1155	0·1154	0·1082	0·1083	3,1,0	W+
0·1350	0·1350	0·1268	0·1267	3,1,1	S−
0·1405	0·1404	0·1321	0·1319	2,1,2	M
0·1421	0·1421	0·1334	0·1333	4,0,0	M
0·1582	0·1582	0·1489	0·1487	3,0,2	S−
0·1619	0·1616	—	—	4,0,1	M+
0·1687	0·1687	0·1581	0·1583	3,2,0	W−
0·1850	0·1850 0·1848	0·1740	0·1739 0·1736	1,0,3 2,2,2,	S−
0·1866	0·1865	0·1749	0·1750	4,1,0	S−
0·1886	0·1883	0·1768	0·1767	3,2,1	S−
0·1938	0·1937	0·1821	0·1819	3,1,2	M
—	—	0·1907	0·1906	1,1,3	M
0·2118	0·2117	0·1992	0·1989	2,0,3	M
0·2201	0·2203	0·2071	0·2069	4,0,2	W+
0·2221	0·2220	—	—	5,0,0	W−
0·2380	0·2382	0·2240	0·2239	2,1,3	M−
0·2414	0·2415	0·2266	0·2267	5,0,1	W
0,2468	0·2470	0·2321	0·2319	3,2,2	W+
—	—	0·2434	0·2434	3,3,1	V.W−
0·2647	0·2647	0·2487	0·2486	4,1,2	M
0·2682	0·2682	0·2516	0·2517	4,2,1	M
0·2915	0·2915	0·2739	0·2739	3,1,3	M−
0·2950	0·2948	0·2767	0·2767	5,1,1	M−
0·3000	0·3002	0·2818	0·2819	5,0,2	W−
0·3130	0·3131	0·2944	0·2943	0,0,4	W−
0 3180	0·3181 0·3180	0·2987	0·2986 0·2989	4,0,3 3,3,2	M−
—	—	0·3029	0·3027	1,0,4	W−
0·3283	0·3285	0·3083	0·3083	4,3.0	W−
0·3397	0·3398	0·3191	0·3193	1,1,4	W−
0·3448	0·3449	0·3242	0·3239	3,2,3	M−
0·3479	0·3481	0·3267	0·3267	4,3,1	M−
—	—	0·3432	0·3434	5,2,1	W−
0·3749	0·3752	0·3523	0·3527	2,1,4	V.W−
0·3931	0·3930	0·3693	0·3693	3,0,4	W−
0·3976	0·3979	0·3738	0·3736	6,0,2	W−
0·4011	0·4014	0·3768	0·3767	6,1,1	W
0·4067	0·4068	0·3819	0·3819	4,3,2	W
0·4194	0·4197	—	—	2,2,4	W−
0·4246	0·4247 0·4246	0·3984	3987 3986	4,2,3 5,2,2	M−
0·4348	0·4351	0·4082	0·4083 0·4083	7,0.0 5,3,0	W
0·4512	0·4513	0·4240	0·4239	5,1,3	W+
0·4544	0·4546 0·4546	0·4266	0·4267 0·4267	7,0,1 5,3,1	W+

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[8] Goroschenko and Andreava, *Russ. J. Inorg. Chem.*, 1963, **4**, 505.

[9] Hayek and Hinterauer, *Monatsh.*, 1951, **82**, 205.

[10] Woolf, *Chem. and Ind.*, 1954, 1320.

EXPERIMENTAL

Work with protactinium was carried out in glove-boxes on account of the radioactive hazards associated with weighable amounts of protactinium-231, the isotope used in this work. The moisture-sensitive compounds were handled in a dry-atmosphere box after isolation.

Solvents.—AnalaR solvents were used and purified as follows: nitrobenzene was fractionated four times under reduced pressure at 158—160°. Ethyl acetate was distilled from phosphorus pentoxide, the middle fraction being retained and redistilled (77—78°). Dioxan was dried by contact with metallic sodium, fractionated at 100—101°, and stored over sodium. The water contents of these solvents were less than 0·04, 0·01, and 0·02%, respectively. Benzene was distilled at 80° and stored over sodium.

Thermogravimetric Results.—These were obtained as described previously.[11] The samples were made into a slurry in anhydrous benzene to afford protection from atmospheric moisture during mounting, the benzene being removed under a vacuum at room temperature before readings were made.

Infrared Spectra.—A Hilger S.P. 800 spectrometer with sodium chloride and cæsium bromide optics was used to measure infrared spectra in the region 2—35 μ. Samples were examined as mulls in Nujol mounted between potassium bromide or Polythene plates.

X-*Ray Powder Diffraction Photographs.*—A Debye-Scherrer 19 cm. camera and a Guinier focussing camera, and filtered Cu-K_α radiation (λ 1·54051 Å) were used. Scales were contact-printed on to the Guinier films before development to counteract film shrinkage during processing.

Solubilities.—These were determined by a combination of α-counting and α-pulse analysis on 10-μl samples, the specific activity of ^{231}Pa being taken as $1{\cdot}047 \times 10^8$ dis./mg./min.

Analytical Methods.—Protactinium was weighed as the pentoxide, Pa_2O_5, after ignition of the hydroxide obtained by treatment of the compounds with aqueous ammonia, or after ignition of the compounds themselves, in air at 750°. Sulphate [12] was determined as barium sulphate after removal of protactium as hydroxide, and potassium was determined by flame photometry.

Owing to the stability of the oxotriselenatoprotactinate(v) towards aqueous ammonia, and the loss of selenium observed during the reduction of selenate to selenite with hydrochloric acid in the presence of hydrofluoric and sulphuric acids, the oxotriselenatoprotactinate(v) was heated in a stream of oxygen at 750° for 1 hr. and the evolved selenium oxides were collected in dilute alkali. The resulting selenate–selenite mixture was then reduced with hydrazine [13] in 4M-hydrochloric acid, and the selenium was weighed as the element. The sulphuric acid eliminated by vacuum decomposition of the trisulphato-complex was titrated against standard sodium hydroxide to the methyl red end-point.

Hydrogen Oxotrisulphatoprotactinate(v).—Protactinium pentoxide (400 mg.) was completely dissolved in 20M-hydrofluoric acid (2 ml.), and concentrated sulphuric acid (2 ml.) was added. The mixture was heated in a platinum crucible under an infrared lamp for several hours to eliminate the fluoride completely; the sulphato-complex crystallised as the latter was removed; after addition of concentrated sulphuric acid (1 ml.) followed by further heating, the crystalline product was isolated by filtration in a dry-atmosphere box. Traces of concentrated sulphuric acid were removed by washing the product with nitrobenzene (2 × 1 ml.), which in turn was removed by washing with benzene (2 × 1 ml.). The solid was dried at room temperature at 10^{-4} mm. for several hours and the last traces of organic solvent were removed under a vacuum by heating at 100° for a short time [Found: Pa, 43·05; SO_4^{2-}, 53·2. $H_3PaO(SO_4)_3$ requires Pa, 42·9; SO_4^{2-}, 53·5%].

Hydrogen Oxotriselenatoprotactinate(v).—Prepared as above, but with selenic acid instead of sulphuric acid, the crystalline product was filtered off and washed with anhydrous ethyl acetate (2 × 1 ml.) to free it from the excess of selenic acid; it was then dried *in vacuo* [Found: Pa, 34·4; Se, 34·85. $H_3PaO(SeO_4)_3$ requires Pa, 34·2; Se, 34·9%].

Hydrogen Oxodisulphatoprotactinate(v).—This was prepared by decomposition of the trisulphato-complex at 375—400° under a vacuum. The decomposition was followed by observing

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[11] Bagnall, Deane, Markin, Robinson, and Stewart, *J.*, 1961, 1611.

[12] Vogel, " A Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 2nd edn., 1951, p. 401.

[13] " Comprehensive Analytical Chemistry," ed. Wilson and Wilson, Elsevier Press, Amsterdam, 1962, Vol. 1C, p. 296.

the pressure changes associated with the evolution of the gaseous decomposition products. This procedure was necessary, since the capacity of the thermogravimetric balance, on which the decomposition was initially observed, was only **30** mg. [Found: Pa, **53·0** ± **1·2**; SO_4^{2-}, **44·3** ± **1·3**; weight loss, 18·0 ± 1. $HPaO(SO_4)_2$ requires Pa, 52·5; SO_4^{2-}, 44·6; weight loss for $H_3PaO(SO_4)_3 \longrightarrow HPaO(SO_4)_2$, 18·2%].

The sulphuric acid eliminated during the above procedure was condensed outside the furnace region and quantitatively recovered from the vessel for analysis (Found: H_2SO_4, 18·7. Required, H_2SO_4, 18·2%).

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