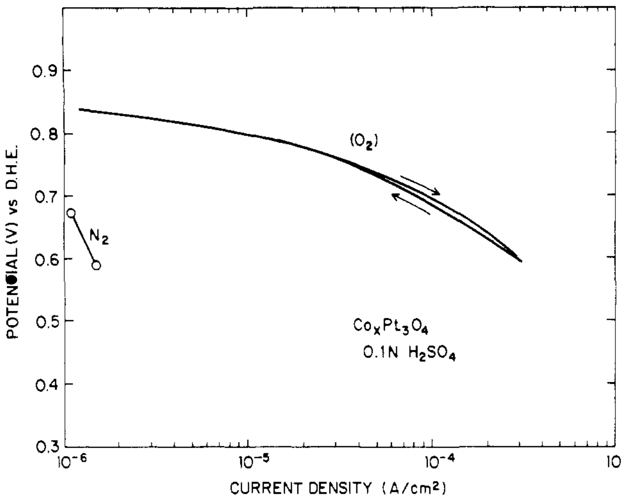

Figure 6. Oxygen reduction current vs. potential for a $Co_xPt_3O_4$ electrode in 0.1 N H_2SO_4 at 23 °C taken at a sweep rate of 0.1 mV/s.

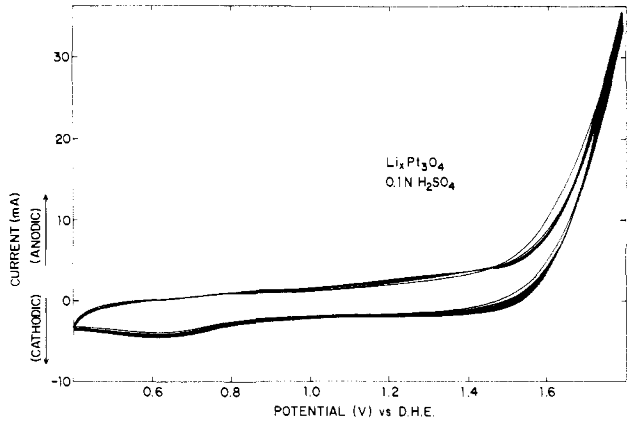

Figure 7. Voltammogram of a $Li_xPt_3O_4$ electrode measured at 20 mV/s sweep rate in 0.1 N H_2SO_4 saturated with N_2 at 23 °C.

below the standard potential of 1.11 V vs. NHE calculated by Nagel and Dietz[62] for a Pt–Pt_3O_4 couple. The measured potentials are substantially below the reversible O_2 potential of 1.23 V vs. NHE, corresponding to the O_2–H_2O reaction

$$O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O \text{ (1.23 V vs. NHE)}$$

They are also well below the 1.06 V vs. NHE mixed potential for Pt[63] and the 1.1 V vs. NHE measured for a Pt–O alloy electrode[64] and suggest that the platinum bronzes may have lower O_2 activity.

The electrocatalytic activity of the platinum bronzes for O_2 reduction has not previously been reported. We have measured high activity for $Li_xPt_3O_4$, $Ni_xPt_3O_4$, and $Co_xPt_3O_4$ electrodes. Figure 6 gives the current-voltage curve in O_2 and N_2 for a $Co_xPt_3O_4$ electrode swept between ~0.85 and 0.65 V vs. DHE at 0.1 mV/s. Similar results were obtained for $Li_xPt_3O_4$ and $Ni_xPt_3O_4$ electrodes. A general characteristic for the platinum bronze electrodes at high potential appears to be a small Tafel slope (~dV/d log i) which increases at lower potentials. For the $Co_xPt_3O_4$ electrode the Tafel slope at high potential is ~50 mV/decade and increases rapidly below ~0.8 V to >150 mV/decade. These features are qualitatively similar to those for O_2 reduction on HNO_3-passivated Pt (Pt–O alloy) electrodes.[64] From capacitance estimates of electrode surface area, the O_2 reduction current density of platinum bronze electrodes is less than for bright Pt.

Figure 7 shows a voltammogram for $Li_xPt_3O_4$ obtained by sweeping the potential at 20 mV/s from 0.4 to 1.8 V vs. DHE. O_2 evolution commences at ~1.4 V, an anodic shoulder occurs at ~0.8 V, and a cathodic peak occurs in the vicinity of 0.65 V in the reverse sweep direction. The voltammogram is qualitatively similar to that measured for Pt_3O_4 by Sukhotin et al.[61] They attributed the cathodic peak to reduction of a surface-oxidized layer. When the $Li_xPt_3O_4$ electrode is swept to a less anodic potential of 1.0 V, no corresponding cathodic peak is detectable in the reverse sweep down to 0.4 V. It is thus likely that the cathodic peak for $Li_xPt_3O_4$ also corresponds to reduction of an oxidized surface layer.

Acknowledgment. We wish to thank C. M. Foris and G. A. Jones for assistance in obtaining the X-ray data, B. F. Burgess and C. R. Perrotto for atomic absorption analysis, J. L. Gillson for resistivity measurements, and A. Ferretti for preparation of some of the $Li_xPt_3O_4$ samples. We are especially grateful to I. McKinnon and C. E. Lyman for the SEM photographs and STEM analyses of $Ni_{0.46}Na_{0.21}Pt_3O_4$ and K. B. Schwartz for assistance in preparation of some of the samples of $Ni_xNa_yPt_3O_4$.

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(61) Sukhotin, A. M.; Gankin, E. A.; Shalman, B. Y. *Zh. Prikl. Khim.* (*Leningrad*) **1972**, *45*, 1484.

(62) Nagel, K.; Dietz, H. *Electrochim. Acta* **1961**, *4*, 141.

(63) Hoare, J. D. *J. Electrochem. Soc.* **1979**, *126*, 1502.

(64) Hoare, J. P. *J. Electrochem. Soc.* **1965**, *112*, 849.

Contribution from the Chemistry Division,
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Synthesis and Characterization of Bis(μ-hydroxo)tetraaquadiplutonium(IV) Sulfate, $Pu_2(OH)_2(SO_4)_3 \cdot 4H_2O$, a Novel Compound Containing Hydrolyzed Plutonium(IV)[1]

DENNIS W. WESTER

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$Pu_2(OH)_2(SO_4)_3 \cdot 4H_2O$ (I) has been synthesized by hydrothermal hydrolysis of plutonium(IV) sulfate solution. I forms as reddish orange crystals at 140 ± 5 °C. Analytical data for Pu (coulometric), SO_4^{2-} (gravimetric), and H_2O (thermogravimetric) are in agreement with theoretical values. X-ray powder diffraction data establish the isomorphicity of I with the Zr, Hf, and Ce analogues. Infrared spectra of I contain the peaks expected for hydroxo, aquo, and sulfato groups. Visible spectra of I are comparable to those for hydrated plutonium(IV) sulfate. Near-infrared spectra of I are reported. Comparisons between tetravalent hydroxysulfate compounds are made.

Hydrothermal hydrolysis of aqueous metal ions frequently leads to compounds with catenated or oligomeric species formed through hydroxo bridges. Among the more common examples are the polymeric hydroxysulfates $M(OH)_2SO_4 \cdot$

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xH_2O (M = Zr, Hf, Th, U, Np, $x = 0$; M = Zr, Hf, $x = 1$; M = Hf, $x = 2$).[2-8] These compounds typically contain infinite chains of stoichiometry $[M(OH)_2]_n^{2n+}$. Another very interesting series of compounds are the $M_2(OH)_2(SO_4)_3 \cdot 4H_2O$ species, where M = Zr, Hf, and Ce. In these compounds, hydrolysis of the aqueous metal ion leads to dimeric $M_2(OH)_2^{6+}$ moieties, which are linked through bridging sulfate groups. The crystal structure of the zirconium compound has been reported previously.[9] The hafnium and cerium analogues were found to be isomorphous to the zirconium derivative.[2a] We now report the synthesis and characterization of $Pu_2(OH)_2(SO_4)_3 \cdot 4H_2O$, which is also isomorphous to the zirconium derivative and represents the first example of a hydrolyzed Pu(IV) compound of well-defined structure.

Experimental Section

All chemicals used were reagent grade, except for plutonium dioxide which was obtained as a green powder from the Special Materials Division of Argonne National Laboratory. The sample of PuO_2 contained 99.91 ± 0.01% $^{242}PuO_2$ according to the original analysis.[10] The remainder of the sample was PuO_2 of other isotopes.

Plutonium dioxide (1.16 g) was dissolved in concentrated hydrobromic acid to which a small amount of hydrofluoric acid (49%) had been added. Evaporation yielded blue crystals, which were dissolved in sulfuric acid (6 M). Hydrogen peroxide (30%) was added dropwise, producing a pink precipitate and a reddish solution. Evaporation and fuming to dryness gave pink $Pu(SO_4)_2$.

Sulfuric acid (0.5 M, 7.5 mL) was saturated with $Pu(SO_4)_2$ and diluted with water (7.5 mL), and the mixture was sealed in a thick-walled Pyrex tube. The tube was placed in a furnace at 140 ± 5 °C for 18 h. After the tube was removed from the furnace, copious reddish orange crystals of $Pu_2(OH)_2(SO_4)_3 \cdot 4H_2O$ (I) were observed in the tube. The tube was opened after cooling. The crystals were separated by filtration, washed with water, and dried in air.

Infrared spectra were run on a Beckman IR10 infrared spectrophotometer. Visible spectra were recorded on a Varian Instruments Cary 17 spectrophotometer. Electrochemical measurements used a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat and a PAR Model 179 digital coulometer. Thermogravimetric analysis was performed on a Mettler thermogravimetric analyzer.

Results and Discussion

The synthesis of $Pu_2(OH)_2(SO_4)_3 \cdot 4H_2O$ (I) employed the technique of hydrothermal hydrolysis. This technique has been used previously to synthesize many compounds, among which are the isomorphous series $M_2(OH)_2(SO_4)_3 \cdot 4H_2O$, where M = Zr, Hf, and Ce.[2a,9] Hydrothermal hydrolysis is readily accomplished by heating a solution which has been sealed in a thick-walled Pyrex tube. For the synthesis of I, a temperature of 140 °C produced copious amounts of reddish orange crystals. Higher temperatures produced a powdery green product, which was analyzed by TGA as 3.5% H_2O and 4.5% SO_3. On the assumption that the remainder of the solid is PuO_2, the empirical formula would correspond closely to $Pu_{12}O_{22}(SO_4)_2(H_2O)_7$. This product gave no distinct X-ray powder diffraction pattern and was not investigated further.

For the analysis of I, a stock solution in perchloric acid (1 M) was prepared. Initial dissolution of I (250.53 mg) in 8 M nitric acid (10 mL) was necessary since acid of lower concentration did not dissolve I. Even with 8 M acid it was necessary to heat the solution in order to achieve a satisfactory rate of dissolution. Evaporation to dryness and dissolution of the solid in perchloric acid gave the desired solution.

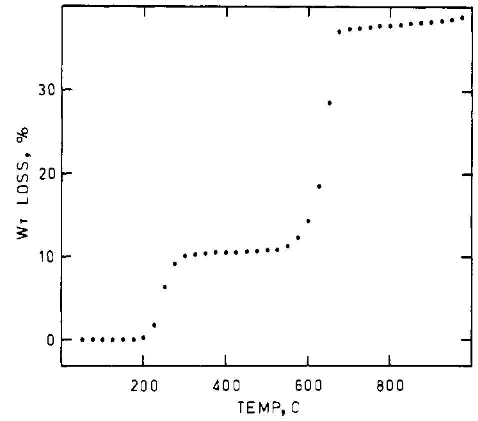

Figure 1. Thermogravimetric analysis of $Pu_2(OH)_2(SO_4)_3 \cdot 4H_2O$ showing weight loss as a function of temperature.

Table I. Analytical Data for $Pu_2(OH)_2(SO_4)_3 \cdot 4H_2O$

	exptl %	theor %
Pu	56.3 ± 2.0	55.1
SO_4	35.8	32.8
H_2O	10.3	10.3

Spectroscopic analysis of this stock solution clearly showed the effect of sulfate complexation in the visible region of the Pu(IV) spectrum. A sharp peak was observed at 479.5 nm. This peak was similar in behavior to one which had been observed previously in dilute sulfuric acid solutions of Pu(IV).[11] The position of this peak is in contrast to the value of 470 nm for Pu(IV) in dilute perchloric acid. However, the uncertainties in both the sulfate concentration and the absorption coefficient for this peak indicated that another method of analysis for Pu was needed.

Coulometric procedures[12] for the analysis of Pu were applied to the stock solution of I. Sulfuric acid (1 M, 25 mL) was preelectrolyzed with a platinum gauze electrode at +0.300 V vs. a saturated calomel electrode (SCE). An aliquot of the stock solution was added to the sulfuric acid, resulting in reduction of all plutonium present to Pu(III). Controlled-potential coulometry at +0.700 V vs. SCE then gave an accurate value for the number of electrons required to oxidize the Pu(III) to Pu(IV). Results of three determinations gave an average value of 56.3 ± 2.0% Pu in the original sample. The procedure employed was advantageous for two main reasons. Primarily, since the procedure depends upon the presence of sulfate to ensure complete reduction of all Pu to the (III) oxidation state, the interference by sulfate, which precluded spectroscopic analysis, was obviated. Secondly, the amount of stock solution required for accurate analysis was relatively small, allowing several determinations. The value obtained, 56.3 ± 2.0% Pu, is in excellent agreement with the theoretical value.

Sulfate determination was accomplished by precipitating barium sulfate and weighing it after drying. The barium used was ca. 0.29 M in perchloric acid (1 M). Barium sufficient to provide a 10-fold excess based on the highest probable sulfate content of I was added. Results of five determinations

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(1) Work performed under the auspices of the Office of Basic Energy Sciences, Division of Nuclear Sciences, U.S. Department of Energy under Contract No. W-31-109-ENG-38.

(2) (a) Rogachev, D. L.; Antsyshkina, A. S.; Porai-Koshits, A. M. *Zh. Strukt. Khim.* **1972**, *13*, 260 and references therein. (b) Hansson, M. *Acta Chem. Scand.* **1973**, *27*, 2455.

(3) Lundgren, G. *Ark. Kemi* **1950**, *2*, 535.

(4) Lundgren, G. *Ark. Kemi* **1952**, *4*, 421.

(5) Wester, D. W.; Mulak, J.; Banks, R.; Carnall, W. T., in press.

(6) Hansson, M. *Acta Chem. Scand.* **1973**, *27*, 2614.

(7) Hansson, M. *Acta Chem. Scand.* **1969**, *23*, 3541.

(8) Hansson, M.; Lundgren, G. *Acta Chem. Scand.* **1968**, *22*, 1683.

(9) McWhan, D. B.; Lundgren, G. *Inorg. Chem.* **1966**, *5*, 284.

(10) Osborne, D. W.; Flotow, H. E. *Phys. Rev. C* **1976**, *14*, 1174.

(11) Lipis, L. V.; Pozharskii, B. G.; Fomin, V. V. *Zh. Strukt. Khim.* **1960**, *1*, 417.

(12) Phillips, G.; Milner, G. W. C. In "Comprehensive Inorganic Chemistry"; Bailar, J. C., Emeleus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: New York, 1973; Vol. 5, p 97.

Table II. Cell Constants for $M_2(OH)_2(SO_4)_3 \cdot 4H_2O$

	M			
	Zr[a]	Hf[a]	Ce[a]	Pu[b]
a, Å	13.056	13.1	13.5	13.51
b, Å	6.5075	6.5	6.7	6.71
c, Å	15.092	15.1	15.8	15.52
β, deg	96.35	96.5	91	95.7

[a] Reference 2a. [b] This work.

gave an average value of 35.5 ± 0.3% SO_4^{2-} in the original sample. It was considered that removal of sulfate from the stock solution by precipitation of $BaSO_4$ might remove the interference in the visible spectrum. However, spectroscopic examination of the sulfate-free stock solution revealed an unusual doublet centered near 475 nm. The spectroscopic examination was not pursued further.

Water analysis was achieved readily through thermogravimetric analysis. Figure 1 depicts the results of this analysis. As the sample is heated, it undergoes two weight changes. The first weight change, which is complete by 300 °C, results in a weight loss of 10.3% of the initial weight. The second weight change, which is essentially complete by 700 °C, results in a weight loss of 28.5% of the initial weight. Figure 1 was constructed in such a manner that comparison with the thermogravimetric data for $Pu(SO_4)_2 \cdot 4H_2O$[13] was facilitated. By analogy with the thermochemistry of $Pu(SO_4)_2 \cdot 4H_2O$, the first weight loss for I is assigned to the loss of water or its equivalent. For example, in $Pu_2(OH)_2(SO_4) \cdot 4H_2O$, there are four water molecules and two hydroxide ions. If the two hydroxides were to convert into one water molecule and one oxide ion, the molecule of water would be detected by TGA. Apparently such a conversion occurs since the TGA data are consistent with the loss of five water molecules per formula weight. The second weight loss is assigned to loss of SO_3 from SO_4^{2-}, again by analogy with $Pu(SO_4)_2 \cdot 4H_2O$. The final residue was assumed to be amorphous PuO_2, since an X-ray powder diffraction pattern of the residue could not be produced.

X-ray diffraction patterns from powdered I were used to establish the isomorphicity among the $M_2(OH)_2(SO_4)_3 \cdot 4H_2O$ compounds where M = Zr, Hf, Ce, and Pu. A set of refined cell constants for I were obtained with use of a locally available computer program. Values for the cell constants of the four compounds appear in Table II. From Table II the similarity between the cell constants for cerium and plutonium is apparent. This similarity is in concordance with that expected on the basis of the effective ionic radii of Ce and Pu, 0.97 and 0.96 Å, respectively.[14] In addition, the similarity between the zirconium and hafnium compounds also is expected on the basis of the similarity of ionic radii for these elements, 0.84 and 0.83 Å, respectively.

Density determinations on I gave results (4.10 ± 0.07 g cm^{-3}) that agreed well with the theoretical value of 4.17 g cm^{-3}. The density of I was determined by the method of Archimedes. For this study, a small crystal of I (typically with a mass 0.75–1.25 mg) was suspended by a thin wire, which had been twisted to form a tiny spiral. The crystal was weighed first in air and then in water. For a reduction in surface tension between the water and the wire, a small amount of a commercially available agent for reduction of surface tension, Kodak Photo-Flo 200 solution, was added. Even so, the method required careful measurement of the weight of the blank in order to yield satisfactory results. Since the crystals often were crudely formed or cracked, a density value slightly lower than the theoretical value is expected.

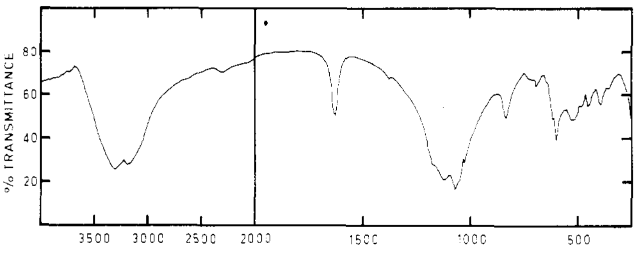

Figure 2. Infrared spectrum of I in a pressed KBr pellet at 298 K.

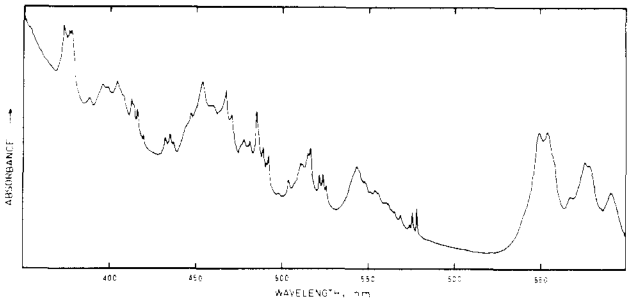

Figure 3. Visible spectrum of I in a pressed KBr pellet at 77 K.

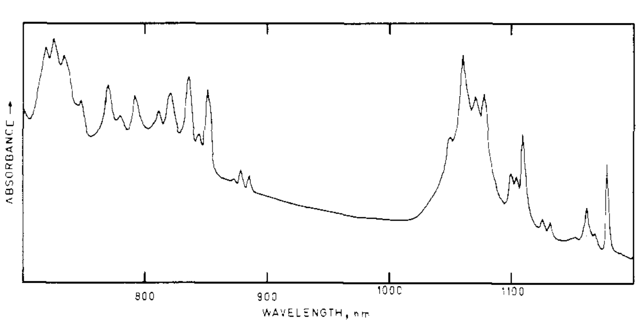

Figure 4. Near-IR spectrum of I in a pressed KBr pellet at 4 K.

The structure of I is assumed to be identical with that of $Zr_2(OH)_2(SO_4)_3 \cdot 4H_2O$[9] except for the expected variations in bond distances. Thus, each plutonium is coordinated to eight oxygens in a dodecahedral arrangement. Four of the oxygens are from bridging sulfate groups, two from water molecules, and two from bridging hydroxide groups. The bridging hydroxide groups are especially interesting since they are situated in such a way that the structure can be viewed as containing dimeric $Pu_2(OH)_2^{6+}$ units. These dimers may then be contrasted with the polymeric species $[M(OH)_2]_n^{2n+}$, which occur in the more extensively hydrolyzed hydroxysulfates $M(OH)_2SO_4$, where M = Zr, Hf, Th, U, and Np. A conclusion that can be drawn is that the $M_2(OH)_2(SO_4)_3 \cdot 4H_2O$ compounds represent a stable phase that is intermediate between the simple hydrated sulfate salts and the extensively hydrolyzed hydroxysulfates. Therefore, the structure of the dimeric hydroxymetal species can be viewed as a step along the route to formation of the Pu(IV) polymer, whose structure is unknown at present.

The infrared spectrum of I, Figure 2, was obtained from a pressed KBr pellet at room temperature. The expected bands for hydroxo, aquo, and sulfato groups are present. The hydroxo stretching band appears at ca. 3320 cm^{-1}. This frequency is similar to that which has been observed for the hydroxysulfates.[5] The stretching and bending bands of water appear at their usual wavenumbers of 3200 and 1641 cm^{-1}, respectively.[15] The sulfate bands, which span the region

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(13) Eichelberger, J. F.; Grove, G. R.; Jones, L. V.; Rembold, E. A. Report MLM-1151, TID-4500, 1963; p 15.

(14) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

(15) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds"; Wiley-Interscience: New York, 1970; p 166.

1000–1200 cm^{-1}, clearly are indicative of bidentate bridging sulfate groups.[15] The fine structure occurring at wavenumbers less than 750 cm^{-1} is unassigned. The bands undoubtedly include a variety of metal–oxygen modes.

The visible spectrum of I, Figure 3, was obtained from a pressed potassium bromide pellet at 77 K. This spectrum is one of the few available for solid-state plutonium compounds. Comparison of the visible spectrum of I with that of $Pu(SO_4)_2{\cdot}4H_2O$[16] does show a remarkable amount of similarity. In particular, the bands between 600 and 700 nm are very similar in shape and relative intensity in both cases. Peaks occurring at higher energies for both compounds are very abundant. The spectra are qualitatively similar although the resolution of the visible spectrum for I is significantly better.

The near-infrared spectrum of I, Figure 4, was obtained from a pressed potassium bromide pellet at 4 K. To the best of our knowledge this is the first report of the near-infrared spectrum for a hydrolyzed Pu(IV) compound in the solid state. Analysis of this spectrum will be attempted at a future date.

Acknowledgment. We wish to thank Dr. Lester R. Morss for his invaluable assistance in obtaining the thermogravimetric analysis. Special thanks are extended to Professor James A. Fahey for his help with the refinement of the cell constants.

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(16) Leontovich, A. M. *Opt. Spektrosk.* **1957**, *2*, 695.

Contribution from the Department of Inorganic Chemistry,
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Oxygen Atom Transfer in Low-Temperature Matrices. 1. Formation and Characterization of Matrix-Isolated OMF_3 (M = P, As)[1a]

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Ultraviolet photolysis of ozone isolated in a noble-gas matrix in the presence of the trifluoride MF_3 (M = P, As) results in the formation of the corresponding trifluoride oxide, OMF_3. The intensities and frequencies of the infrared absorptions due to the ^{16}O- and ^{18}O-substituted versions of the hitherto unknown molecule $OAsF_3$ are consistent with the expected C_{3v} symmetry. The vibrational spectra have been analyzed for information about the bonding in $OAsF_3$, and an attempt has been made to estimate the bond angles on the basis of the intensities in infrared absorption of the bond-stretching fundamentals.

Introduction

Although trifluoramine oxide[2] and the phosphorus trihalide oxides, OPX_3 (X = F, Cl, Br),[3] are well-characterized, surprisingly little is known about the analogous compounds of arsenic, antimony, and bismuth. It is quite possible that the formation of these compounds, like that of perbromates,[4] is hampered as much by kinetic as by thermodynamic barriers. It is also possible that the discrete molecular species characteristic, for example, of the phosphorus trihalide oxides[3] give place in the corresponding derivatives of the heavier elements at normal temperatures and pressure to oligomeric or polymeric aggregates. The significance of this last point is underlined by the brief but checkered history of arsenic trifluoride oxide. Thus a product with the composition $OAsF_3$ formed by thermal decomposition of the fluoride nitrate $AsF_3(NO_3)_2$ is described as a "white hygroscopic solid" involatile at ambient temperatures;[5] on the other hand, fluorination of an equimolar mixture of arsenic(III) chloride and arsenic(III) oxide is claimed elsewhere[6] to give a product also with this composition, which is a liquid with a boiling point of 26 °C.

The experience gained in several laboratories testifies to the feasibility of inducing oxygen atom transfer to a suitable molecular substrate by ultraviolet photolysis of ozone coexisting in a noble-gas matrix. Hence, for example, the molecules OClF[7] and HOX (X = Cl,[8] Br,[8] I[9]) have been generated from the substrates ClF and HX, respectively. Experiments carried out in this laboratory demonstrate that the matrix reaction

$$O_3 + D \xrightarrow{h\nu} DO + O_2$$

can also be enacted with either a group 5 trihalide[10,11] or iodine monochloride[12] as the donor partner D. We have established, for instance, that the hitherto unknown arsenic trichloride oxide, $OAsCl_3$, is formed by ultraviolet photolysis of a noble-gas matrix containing ozone and arsenic trichloride.[10,11] Seppelt and his co-workers[13] have exploited thermal rather than photolytic activation of the reaction between ozone and arsenic trichloride to synthesize arsenic trichloride oxide on a larger scale and so characterize it as a molecular solid stable at temperatures up to ca. −30 °C. They have also noted that ozone and arsenic trifluoride do not react in comparable circumstances.

In this paper we describe the formation of the molecules OPF_3 and $OAsF_3$ by ultraviolet photolysis of ozone supported in a noble-gas matrix doped with the appropriate trifluoride. We have witnessed the reaction and characterized each of the

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(1) (a) Presented in part at the 6th European Symposium on Fluorine Chemistry, Dortmund, West Germany, March–April 1977. (b) Present address: Esso Research Centre, Abingdon, Oxfordshire OX13 6AE, England.

(2) Fox, W. B.; MacKenzie, J. S.; McCarthy, E. R.; Holmes, J. R.; Stahl, R. F.; Juurik, R. *Inorg. Chem.* **1968**, *7*, 2064. Plato, V.; Hartford, W. D.; Hedberg, K. *J. Chem. Phys.* **1970**, *53*, 3488.

(3) Toy, A. D. F. "The Chemistry of Phosphorus"; Pergamon Press: Oxford, 1975; p 430.

(4) Appelman, E. H. *Acc. Chem. Res.* **1973**, *6*, 113.

(5) Dehnicke, K.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1966**, *342*, 225.

(6) Mitra, G. *J. Am. Chem. Soc.* **1958**, *80*, 5639.

(7) Andrews, L.; Chi, F. K.; Arkell, A. *J. Am. Chem. Soc.* **1974**, *96*, 1997.

(8) Schwager, I.; Arkell, A. *J. Am. Chem. Soc.* **1967**, *89*, 6006.

(9) Walker, N.; Tevault, D. E.; Smardzewski, R. R. *J. Chem. Phys.* **1978**, *69*, 564.

(10) Gaskill, G. P. D.Phil. Thesis, University of Oxford, 1978. Downs, A. J.; Gaskill, G. P.; Saville, S. B., unpublished results.

(11) Downs, A. J.; Gaskill, G. P. *Proc. Int. Conf. Raman Spectrosc. 5th* **1976**, 130. Benfield, F. W. S.; Downs, A. J.; Gaskill, G. P.; Staniforth, S. E. *J. Chem. Soc., Chem. Commun.* **1976**, 856.

(12) Drury, D. J. D.Phil. Thesis, University of Oxford, 1979. Downs, A. J.; Drury, D. J., unpublished results.

(13) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 766. Seppelt, K.; Lentz, D.; Eysel, H.-H. *Z. Anorg. Allg. Chem.* **1978**, *439*, 5.