which are formally Yb(II) and Yb(III). One difficulty in the proposed esr studies with $YbH_{2.55}$ might lie in finding an isostructural diamagnetic material with which to dilute it, if necessary, although lutetium hydride offers one possibility. Oxide systems offer a parallel.[20] In $YbH_{2.55}$, 55% of the ytterbium atoms are formally Yb(III) and the material exhibits a corresponding magnetic susceptibility.

The CaF_2–YF_3 system[21] resembles the LaH_2–LaH_3 and YbH_2–YbH_3 systems with regard to the occupation of the octahedral sites. These sites are filled at random in the LaH_2–LaH_3 instance, but in an ordered manner in the YbH_2–YbH_3 case (*vide infra*). Considering a composition $YbH_{2.500}$, half of the octahedral sites are filled, and a superstructure is possible whose unit cell consists of eight of the smaller unit cells with $a = 5.19$ A. Such a superstructure, containing hydride ions in every other octahedral site, would be detectable by neutron diffraction. It would appear that a necessary consequence of the existence of plateaus in the pressure–composition isotherms, for the region richer in hydrogen than YbH_2, is that the hydrogen-rich phase has the ordered superstructure. In $YbH_{2.55}$, the hydrogen atoms beyond $YbH_{2.50}$ probably enter octahedral sites at random. Neutron diffraction techniques might also provide evidence on the equivalence of the ytterbium atoms in $YbH_{2.55}$, as in the case of certain oxides.[22] Crystal field deformations resulting from the Yb(III) are expected to be negligible.

Assuming a single phase containing ytterbium of average oxidation number 2.5, the calculated lattice constant would be 5.18 A if average radii of Yb^{2+} (1.05 A) and Yb^{3+} (0.868 A) are used, compared with the observed 5.19 A. When a one-phase material above 320°, of composition $YbH_{2.2}$, for example, is cooled, it disproportionates into fcc YbH_2 and another phase richer in hydrogen. This second phase is $YbH_{2.25}$ at 300°, $YbH_{2.46}$ at 260°, and $YbH_{2.55}$ at 25°. This material is formed rather than a hydrogen-deficient hexagonal YbH_3 because the resonance effects generate thermodynamic stability, relative to YbH_3. In pure YbH_2 also, the metal ions are all identical through resonance, or exchange *via* conduction electrons.

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(21) J. Short and R. Roy, *J. Phys. Chem.*, **67**, 1860 (1963).

(22) C. G. Shull and E. O. Wollan, *Solid State Phys.*, **2**, 137 (1956).

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Americium(III) Perxenate[1]

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Americium perxenate has been prepared by precipitation from basic solutions of americium(III). The compound is orange and shows the characteristic absorption bands of Am(III) in the visible and near-infrared regions, as well as the characteristic infrared absorption at 650–680 cm^{-1} for the Xe–O vibration in perxenate. The compound is highly hydrated and has the stoichiometric composition $Am_4(XeO_6)_3 \cdot 40H_2O$. Its solubility in water is 4.6×10^{-5} *M*. The compound dissolves in acid to form Am(VI) and Am(V).

Introduction

Am(III) in aqueous solutions can be oxidized by strong oxidants to the penta- or hexavalent state. In acid solutions, the formal oxidation potentials are 1.75 v for Am(III)–Am(VI) and 1.83 v for Am(III)–Am(V).[2] The oxidation potentials in basic solutions are unknown, but americium(III) hydroxide in suspension is readily oxidized by hypochlorite to americium(IV) hydroxide.[3] Ozone and persulfate oxidize Am(III) in hydroxide suspensions and in carbonate solutions to the penta- and hexavalent states.[3,4] It is of interest to examine the action of the new powerful oxidation agent, sodium perxenate,[5] which is effective in acid, neutral, or basic solutions. In acid solutions, indeed, plutonium(III) has recently been found[6] to be oxidized to Pu(IV) by "xenic acid," *i.e.*, hydrated XeO_3, quite rapidly, and Pu(IV) can be further oxidized to Pu(VI). The normal oxidation potentials in 1 *M* acid are 0.91 v for Pu(III)–Pu(IV) and 1.05 v for Pu(IV)–Pu(VI).[7] Oxidation of actinide ions in basic solutions by perxenate has not yet been reported. Sodium perxenate[5] is a white crystalline powder which exists as an anhydrous salt or may contain up to eight

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission, presented in part at the XXXVth meeting of the Israel Chemical Society.

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molecules of water per xenon. Its solubility in water is 0.025 *M* and it is much less soluble in basic solutions. Aqueous perxenate solutions decompose yielding oxygen and Xe(VI). At pH 11.5 the decomposition is about 1%/hr, at pH 8 the rate exceeds 1%/min, and below pH 7 decomposition is practically instantaneous. At pH 12, sodium perxenate is hydrolyzed to yield $HXeO_6^{3-}$ and OH^- ions, while Xe(VI) is present as $HXeO_4^-$. The formal potential of Xe(VI)-Xe(VIII) is 0.9 v in basic solution and 3.0 v in acid solution.

Gruen[8] has reported on perxenates of lead, silver, and uranyl ions. However, these solids were not characterized. Appelman and Malm[9] mention solid perxenates of Th^{4+}, La^{3+}, and Zn^{2+}, but again give no details.

This work explores the conditions under which Am(III) is oxidized by perxenate and under which Am(III) perxenate is obtained. The solid perxenate is established by several methods.

Experimental Section

Materials.—The americium used had the isotope Am^{243} ($t_{1/2}$ = 7.95 × 10^3 years) as its main component, constituting 84.3 ± 1.5% of the total α activity (the rest being Cm^{244} and Am^{241}). According to the counting geometry used, this corresponds to 3.75 ± 0.08 μg per 10^5 counts/min. Sodium perxenate was obtained from Dr. H. Selig of this laboratory. Ozone was used at a concentration of ~2% in oxygen. All other chemicals were of analytical reagent quality.

Instruments.—Absorption spectra in the visible and near-infrared regions were obtained on a Cary Model 14 recording spectrophotometer. Spectra of solids were taken with Nujol mulls, between two quartz plates. Infrared spectra were obtained on a Beckman IR-10 machine; spectra were obtained in Nujol or Fluorolube mulls, or in potassium bromide pellets.

Analysis.—A portion of a thoroughly washed and vacuum-dried precipitate of americium(III) perxenate was dissolved in aqueous sodium iodide, approximately 0.05 *M*. This solution was subsequently made about 0.04 *M* in hydrochloric acid, in order to cause the liberation of the iodine, and finally made up to a known volume with water. An aliquot, diluted appropriately and plated, was counted to give the amount of americium in the sample. In other aliquots, the amount of iodine liberated was determined by titration with 0.0100 *N* sodium thiosulfate in the usual manner. This titration gives the total oxidizing power of the sample.[5] The relative concentrations of Am in the different oxidation states were obtained spectrophotometrically within *ca.* 5 min of the acid dissolution. The molar extinction coefficients (M cm^{-1}) used are: Am(III), ϵ 380 at 503 mμ; Am(V), ϵ 55 at 718 mμ; and Am(VI), ϵ 75 at 995 mμ.

Results

Americium(III) perxenate was prepared by precipitation of Am(III) in carbonate solutions by the addition of solid sodium perxenate. The color of the precipitate is orange when wet, and when dried under vacuum at room temperature, or in air on a boiling water bath, it becomes orange-tan. The precipitate can be water-washed without decomposition or loss by solubilization. The solubility of americium(III) perxenate in distilled water at room temperature (~23°) is 4.6 × 10^{-5} *M* (relative to americium).

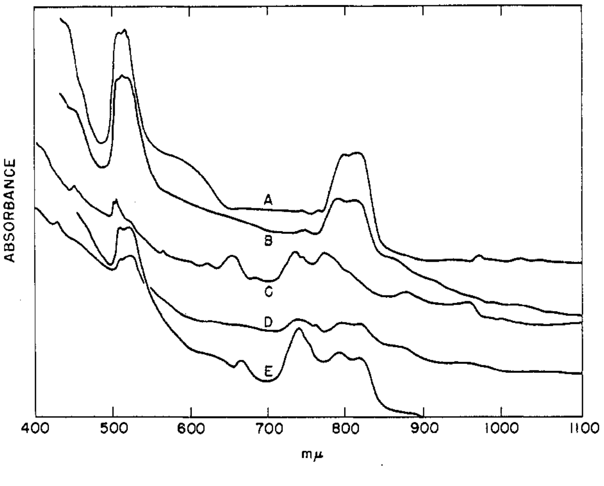

Figure 1.—Absorption spectra of americium(III) perxenate preparations in the visible and near-infrared regions: curve A, precipitated from 3.8 *M* K_2CO_3; curve B, precipitated from 2.0 *M* Na_2CO_3; curve C, precipitated by ozone from 3.8 *M* K_2CO_3 (no perxenate added); curve D, precipitated from 0.225 *M* $Na_4P_2O_7$; curve E, precipitated from 2 *M* $NaCH_3CO_2$ + 1 *M* HCH_3CO_2.

The analytical results from two samples lead to the formulation of the stoichiometry of the precipitated compound as $Am^{III}(Xe^{VIII}O_6)_{3/4}\cdot 10H_2O$. *Anal.* Calcd: Am, 41.0; oxidizing power, 10.1 μequiv/mg. Found: Am, 41.5 ± 0.3; oxidizing power, 10.2 ± 0.6 μequiv/mg. The degree of hydration is obtained by difference.

In order to characterize the compound further, absorption spectra were measured. The visible spectrum is shown in Figure 1, curves A and B, where bands near 520 and 810 mμ, characteristic of Am(III), are seen. No prominent peaks attributable to Am(V) or Am(VI) are found. It should, however, be noted that the bands show some structure and that their center of gravity is shifted from the positions of the peaks of Am(III) in dilute aqueous solutions. The 520 mμ band has a peak at 518 mμ, a shoulder at 511 mμ, and another peak, or shoulder, at 525 mμ; the 810 mμ band has a broad peak at 790–798 mμ and another at 816 mμ.

The absorption spectrum of this compound does not correspond to that of Am(V). A sample of potassium americyl(V) carbonate, $KAmO_2CO_3$, prepared by oxidation of Am(III) in 3.8 *M* potassium carbonate by ozone, was examined spectrophotometrically. The dirty, pale yellow precipitate has the spectrum shown in curve C in Figure 1. It lacks the peak at 800–820 mμ characteristic of Am(III) and shows bands with some structure at 510 and 735 mμ (corresponding to 514 and 718 mμ in aqueous Am(V)), as well as peaks at 620, 655, 755, 870, and 950 mμ.

The material produced by ozone oxidation, when dissolved in dilute acid, produced 95% Am(V), while the material precipitated from the same solution by perxenate produced mixtures of Am(III), Am(V), and Am(VI) (see below) and is thus definitely not an americium(V) carbonate.

The infrared spectrum is reproduced in Figure 2, curve A, for a Nujol mull (a mull in Fluorolube has given a practically identical spectrum) and in curve

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[8] D. M. Gruen in "Noble Gas Compounds," H. H. Hyman, Ed., Chicago University Press, Chicago, Ill., 1963, p 174.

[9] E. H. Appelman and J. G. Malm in "Preparative Inorganic Reactions," Vol. 2, W. L. Jolly, Ed., Interscience Publishers, New York, N. Y., 1965, p 347.

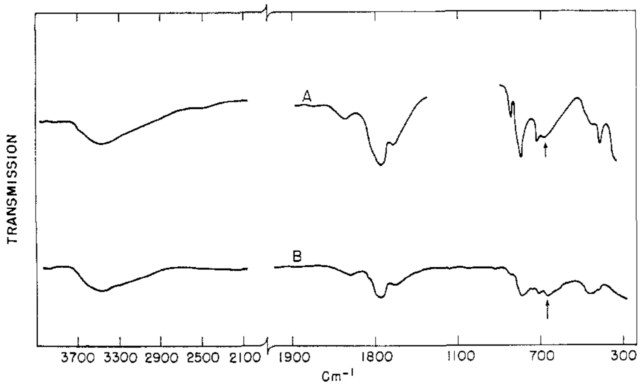

Figure 2.—Infrared absorption spectra of americium(III) perxenate precipitated from K_2CO_3 solutions: curve A, Nujol mull (absorption by Nujol subtracted); curve B, KBr disk.

B for a potassium bromide pellet. Both curves show a band around 3400 cm^{-1} and another around 1650 cm^{-1}, which can be attributed to absorption by water, present in the vacuum-dried material. There is another band at 670–690 cm^{-1}, attributable to the ν_3 mode of the XeO_6 octahedral grouping of the perxenate anion.[8] In addition, both curves show peaks at 1480, 1420, 840, 790, 720, and 420 cm^{-1} and shoulders at 1390 and 460 cm^{-1}. Absorption at or near 900 cm^{-1}, characteristic of the O–Am–O asymmetric vibration of Am(VI),[10] is absent.

The dissolution of americium(III) perxenate in acid is accompanied by decomposition and bubble formation. The decomposition products from material prepared in carbonate solutions (sodium or potassium) and dissolved in 0.2 *M* nitric acid are mainly xenon gas, Am(V), and Am(VI), with little contamination by Am(III) (Table I). The average oxidation number of the americium in these solutions is 5.4–5.7. Evidently, the perxenate anion on acidification oxidizes the americium to the higher oxidation state, the exact oxidation state of the product depending somewhat on the conditions.

Table I

Products of Acid Dissolution of Precipitates Prepared in Various Media

Medium	% Am III	% Am V	% Am VI	Av oxidn no.
K_2CO_3 (3.8 *M*)	4.0	38.5	57.5	5.49
K_2CO_3 (3.8 *M*)	3.0	35.0	62.0	5.56
K_2CO_3 (0.8 *M*)	1.5	23.0	75.5	5.73
Na_2CO_3 (2.0 *M*)	2.5	49.5	48.0	5.44
Na_2CO_3 (2.0 *M*)	12.0	52.5	35.5	5.12
$Na_4P_2O_7$ (0.23 *M*)	19.0	15.5	65.5	5.58
$Na_4P_2O_7$ (0.23 *M*)	34.0	10.0	56.0	4.88
$NaCH_3COO$ (4 *M*, pH 9)	7.5	13.5	79.0	5.74
$NaCH_3COO$ (4 *M*, pH 7)	27.0	18.5	54.5	5.01
(Na,H)CH_3COO (3 *M*)	55.0	0.0	45.0	4.35
NaOH	61.0	13.5	25.5	4.04
K_2CO_3, ozone	5.0	95.0	0.0	4.90

Americium(III) perxenate can be prepared under a variety of conditions. The materials precipitated from 3.8 or 0.8 *M* potassium carbonate or 2.0 *M* sodium carbonate solutions are apparently the same, relatively pure americium(III) perxenate (*cf.* Figure 1 and Table I).

From a solution of the white precipitate, formed on the addition of 0.225 *M* sodium pyrophosphate to a solution of Am(III) in 0.20 *M* nitric acid, in excess 0.225 *M* sodium pyrophosphate, americium(III) perxenate is precipitated and is contaminated with Am(V), possibly as the pyrophosphate. The absorption spectrum of a mull of this precipitate, curve D of Figure 1, shows this contamination, exhibiting a band with a peak at 740 mμ and a shoulder at 762 mμ, in addition to the bands shown by americium(III) perxenate (curves A and B). When dissolved in acid, however, most of the Am(V) disproportionates, and relatively more Am(III) results in the solution than from material precipitated from carbonate solutions, while the average oxidation number is comparable (Table I).

The precipitate formed from Am(III) in saturated sodium acetate solutions (about 4 *M*, pH ~9) is very similar to that formed in carbonate solutions and yields similar products on acidification (Table I). When the solution is initially at a somewhat lower pH (pH ~7), more Am(III) and Am(V) appear in the dissolution products, and the average oxidation number decreases. Finally, from a solution which is 3.0 *M* in acetate, but also 1.0 *M* in acid, a precipitate is formed (Figure 1, curve E) which contains appreciable quantities of Am(V) and possibly also some Am(VI) (perhaps as sodium americyl(VI) acetate), along with americium(III) perxenate, as shown by the peaks at 740 (with a shoulder at 755 mμ) and 665 mμ. When dissolved in acid, this precipitate yields Am(III) and Am(VI) only, and an average oxidation number of 4.35 (Table I).

It appears from the above that the more basic the solution, the higher the yield of pure americium(III) perxenate, but this is not completely so. A suspension of americium(III) hydroxide in either 4.0 *M* sodium hydroxide or 0.8 *M* potassium carbonate–3.2 *M* sodium hydroxide was oxidized by sodium perxenate slowly to a blackish brown precipitate. When washed thoroughly with water, it dissolved in 0.2 *M* nitric acid without bubble formation, showing the absence of perxenate in the precipitate. It gave a solution with an average oxidation number of 4.04 (Table I), characteristic of solutions in acid of americium(IV) hydroxide,[3] which the precipitate resembled in appearance.

Discussion

The results shown above give a reasonable assurance that the compound prepared is indeed americium(III) perxenate. The formulation $Am_4(XeO_6)_3 \cdot 40H_2O$ fits the data, whereas other formulations, such as $AmHXeO_6 \cdot 10H_2O$ or $Am_2(XeO_4)_3 \cdot 20\ H_2O$, do not.

The high degree of hydration for this compound is unusual. Although there is a sodium perxenate with eight[5] molecules of water and a potassium perxenate

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[10] L. H. Jones, *J. Chem. Phys.*, **21**, 542 (1953).

with nine[11] molecules of water per xenon, these crystals are "wet," not dried solids as in the case of americium perxenate. Further work will be necessary to check this unusual high degree of hydration.

Some preliminary work has been started with studying rare earth perxenates. For example praseodymium perxenate is a green insoluble solid. It "pops" when heated on a spatula. Its infrared spectrum is similar to that of americium perxenate. However, the hydration of this salt has not as yet been studied.

The solubility[9] of the perxenates decreases in the sequence $\mathrm{Na^+}$ (2.5×10^{-2} *M*) > $\mathrm{Li^+}$ (1.0×10^{-3} *M*) > $\mathrm{Am^{3+}}$ (6.1×10^{-5} *M*) > $\mathrm{Ba^{2+}}$ (2.3×10^{-5} *M*).

This study does not answer the problem of the oxidation of Am(III) in acid solutions by xenate or perxenate. A high yield (up to 80%) of Am(VI) has, however, been attained on the acid dissolution of the americium(III) perxenate prepared in basic solutions.

(11) A. Zalkin, J. D. Forrester, D. H. Templeton, S. Williamson, and C. W. Koch, *J. Am. Chem. Soc.*, **86**, 3569 (1964).

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Environmental Effects on f–f Transitions.[1] I. Neodymium(III)

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The changes in the absorption spectrum (visible and near-infrared) of neodymium(III) have been studied in various media. It has been found that ligands may be divided into groups based upon their effect on the spectrum. The ligands within each group share certain chemical and physical characteristics suggesting that covalent effects are important for complexes of the rare earths. The use of spectral modifications to differentiate between inner- and outer-sphere complexes is discussed, and the behavior of the "hypersensitive" $^4I_{9/2} \longrightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition is discussed in relation to recent hypotheses concerning the origin of this effect.

Introduction

The correlation between structure and absorption spectra for complexes of the transition metals is rather well understood in terms of the ligand field theory. Regrettably, the same situation is not true for complexes of the lanthanide and actinide metals. It is well-known that the visible and near-infrared absorption spectra, consisting of narrow bands due to electronic transitions (Laporte forbidden) within the f^n configuration, are affected only slightly by changes in the environment of the metal ion. This is attributed to the shielding effect on the f electrons by the outer electrons of the ion.

The observed frequency changes are of the order of a few per cent,[3,4] while certain band intensities change by factors of 2 to 4.[5] Stark splittings due to a ligand field plus changing intensities give rise to marked variations in band shape. Moreover, interpretation of the spectra of rare earth ions in aqueous solutions is often greatly complicated by the simultaneous occurrence of several complex species. Only in the cases of well-defined complexes can certain conclusions be drawn from the absorption spectra concerning structure.

Recent theoretical work[6,7] has made variations in intensity more susceptible to interpretation. This study concerns the environmental effects on the spectrum of Nd(III) in an attempt to discover possible systematic effects connected with inner- and outer-sphere complex formation, anionic complexes attached to ion exchangers, and structural similarities of ligands. The variation in the intensity of the "hypersensitive" transition $^4I_{9/2} \rightarrow {}^4G_{5/2}$ is discussed in relation to the theory of Judd and Jørgensen[3] as to the origin of these effects. The neodymium acetate system is emphasized since by using the stability constants a more complete analysis was feasible. Other systems, where such an analysis is not at present possible, are discussed more qualitatively.

Experimental Section

The spectral measurements were made using a Cary Model 14 spectrophotometer and both 1- and 5-cm fused silica cells. All chemicals were reagent grade materials. The Nd(III) concentration in the aqueous solutions was approximately 0.015 *M* for all systems but acetate, where the concentration was 0.067 *M*. The trinonylamine (TNA) was dissolved in ether (40% solution for $\mathrm{Cl^-}$ and $\mathrm{SCN^-}$, 20% for $\mathrm{NO_3^-}$). As anion-exchange resin, Dowex 1X1 was used. Saturated solutions of salts of the complexing anions, containing Nd(III), were run through a small column of Dowex 1X1 until the resin by visual estimation contained the appropriate amount of Nd(III). In cases where the complex is strongly held by the resin (such as with nitrate com-

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(2) (a) Florida State University; (b) Euratom.

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(6) B. R. Judd, *Phys. Rev.*, **127**, 750 (1962).

(7) G. S. Oefelt, *J. Chem. Phys.*, **37**, 511 (1962).