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Preparation and Properties of Americium(VI) in Aqueous Carbonate Solutions[1]

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Hexavalent americium is conveniently prepared as a soluble, red-brown complex in aqueous Na_2CO_3 or $NaHCO_3$ by O_3 or $S_2O_8^{-2}$ oxidation of americium in lower valence states. The solutions in 0.1 to 0.5 *M* $NaHCO_3$ are stable at 90° to reduction by H_2O, Cl^-, and Br^-, but are readily reduced by I^-, N_2H_4, H_2O_2, NO_2^-, and NH_2OH. Reduction by water occurs at 90° in 2 *M* Na_2CO_3. The spectra of Am(VI) in the 500–1300 mμ region are markedly different in carbonate solutions than in acid. The infrared spectra of solid sodium americyl(VI) carbonates establish the presence of the O–Am–O group in the carbonate complex. Based on the properties of Am(VI) in carbonate solution, a new procedure for the preparation of Am(V) free from traces of Am(III) and a useful process for the separation of americium and curium are reported.

Introduction

In the dozen years since the existence of hexavalent americium was first established, it has been shown to exist in acid solution as the AmO_2^{++} ion, its exchange reactions with other americium ions have been studied, the rate of autoreduction of Am^{241}(VI) has been measured, and the potential of the Am(V)–Am(VI) couple has been determined.[3,4] Most of the other aspects of the chemistry of Am(VI) remain to be explored.

The present study was undertaken to examine the behavior of Am(VI) in a strongly complexing medium. Carbonate solutions were chosen since Am(VI) was reported to be stable in carbonate solution and to form a highly colored complex.[5] In addition, preliminary experiments indicated that oxidation of americium to species soluble in carbonate would be useful in the purification and preparative chemistry of americium.

Experimental

Preparation of Am(VI) in $NaHCO_3$–Na_2CO_3 Solutions.—Oxidation of either Am(III) or Am(V) with O_3 or $Na_2S_2O_8$ in $NaHCO_3$ gives solutions of Am(VI) having an intense and characteristic red-brown color.

(1) **Oxidation of Am(III).**—In a typical preparation, 5–10 mg. of $Am(OH)_3$ is slurried with 5 ml. of 0.1 *M* $NaHCO_3$. Oxygen containing *ca.* 5% O_3 is bubbled through the slurry for 1 hr. Quantitative oxidation to Am(VI) is obtained at any temperature in the range 0–90°. Ozone concentration must be several per cent for successful oxidation.

Ozone oxidation of Am(III) dissolved in 2 *M* Na_2CO_3 yields red-brown Am(VI) *only* if the temperature is maintained at room temperature or below. At 90° americium oxidation does not proceed past Am(V). In fact, when Am(VI) in 2 *M* Na_2CO_3 (previously prepared at a lower temperature) is heated to 90° even with O_3 present, it is largely reduced to Am(V) within 60 min. and sodium americyl(V) carbonate is precipitated. In contrast, Am(VI) can be maintained at 90° in 2 *M* Na_2CO_3 in the presence of 0.01 *M* $Na_2S_2O_8$.

(2) **Oxidation of Am(V).**—Sodium americyl(V) carbonate is readily oxidized to Am(VI) by O_3 at room temperature or by 0.01 *M* $Na_2S_2O_8$ at 90° in $NaHCO_3$ solutions $\leqq$ 1 *M*.

Oxidation with NaOCl of sodium americyl(V) carbonate (and of $Am(OH)_3$) was attempted without success in 0.1 *M* and in 1 *M* $NaHCO_3$ at 90°.

(3) **Dissolution of Sodium Americyl(VI) Acetate in $NaHCO_3$–Na_2CO_3 Solutions.**—Yellow-green sodium americyl(VI) acetate is readily precipitated by saturation of a faintly acid solution of Am(VI) with sodium acetate. Dissolution of the precipitate in aqueous $NaHCO_3$ or Na_2CO_3 yields intense red-brown solutions of Am(VI). No indication of reduction of Am(VI) to Am(V) has been observed during this procedure.

Titration with Hydrazine Sulfate.—Quantitative evidence for the existence of americium in oxidation state (VI) in the red-brown carbonate solution was obtained by titration with hydrazine sulfate to the point of disappearance of the red-brown color. The reduction proceeds rapidly at room temperature and results in precipitation of sodium americyl(V) carbonate. Total americium was determined radiometrically. Titration of four separate solutions prepared by ozone oxidation of $Am(OH)_3$ in 0.1–0.2 *M* $NaHCO_3$ established that 1.0 ± 0.1 equivalent of hydrazine is consumed per mole of americium reduced to Am(V).

Oxidation of Americium in $KHCO_3$–K_2CO_3 Solutions.—A striking *difference* in behavior is observed when potassium is substituted for sodium in the bicarbonate–carbonate system. Americium(VI) is *not* produced by ozone oxidation of $Am(OH)_3$ or potassium americyl(V) carbonate in 0.03–0.1 *M* $KHCO_3$ solutions. Similarly, attempted oxidation of $Am(OH)_3$ and of sodium americyl(V) carbonate in 0.1 *M* $NaHCO_3$ produced no Am(VI) when *potassium* peroxydisulfate was used as oxidant (though oxidation to Am(VI) is rapid and complete with *sodium* peroxydisulfate). Further, addition of $KClO_4$ to a solution of Am(VI) in 0.1 *M* $NaHCO_3$ led, after heating for 5 min. at 90°, to precipitation of potassium americyl(V) carbonate.

The new compound produced by O_3 oxidation of $Am(OH)_3$ in 0.03 *M* $KHCO_3$ has been identified as $KAmO_2CO_3$. Its X-ray powder pattern shows it to be hexagonal and isostructural with the known compounds $RbAmO_2CO_3$ and $KPuO_2CO_3$.[6,7]

Spectra in the 500–1300 mμ Region.—The spectrum of Am(VI) prepared by dissolving sodium americyl(VI) acetate in 0.1 *M* Na_2CO_3 is shown in Fig. 1. The spectrum of a solution prepared by O_3 oxidation of $Am(OH)_3$ in 0.1 *M* $NaHCO_3$ was essentially identical. These spectra bear almost no resemblance to the spectra of Am(VI) in acid solution.

No color change is observed upon making millimolar Am(VI) solutions in 0.1 *M* $NaHCO_3$ up to 2 *M* in sodium acetate or NH_4F, or 1 *M* in NaCl, NaBr, or Na_2SO_4. However, addition of NaOH causes an immediate color change from intense red-brown to yellow. At low americium concentrations the Am(VI) remains

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[3] J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," John Wiley and Sons, New York, N. Y., 1957, pp. 331–372.

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[6] J. P. Nigon, R. A. Penneman, E. Staritzky, T. K. Keenan, and L. B. Asprey, *J. Phys. Chem.*, **58**, 403 (1954).

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in solution. Addition of $NaHCO_3$ to the NaOH solution of Am(VI) restores the Am(VI) carbonate color. The spectra of Am(VI) in hydroxide solutions are poorly reproducible but clearly differ from those in either acid or carbonate.

One other alkaline complexing agent, pyrophosphate, was found to stabilize Am(VI). In contrast to carbonate, the spectrum of Am(VI) in 0.1 *M* $Na_4P_2O_7$ (Fig. 2) is similar in general appearance to that of AmO_2^{++} in acid solution. In a solution containing equal concentrations (0.1 *M*) of Na_2CO_3 and $Na_4P_2O_7$, the spectrum shows that both complexes are present.

Stability and Other Properties of Am(VI) in $NaHCO_3$–Na_2CO_3 Solutions. (1) Radiolytic Reduction.—In $NaHCO_3$ or Na_2CO_3 solutions, reduction of Am(VI) to Am(V) occurs as a result of the Am^{241} α-radiation and the intense color due to Am(VI) is discharged within approximately 1 day. This is consistent with the self-reduction rates of about 4%/hr. typically observed in acid solution. An absorption peak at about 730 mμ due to Am(V) increases as the self-reduction proceeds. Precipitation of sodium americyl(V) carbonate usually is observed as self-reduction approaches completion, but the solubility of this compound is sufficiently high that the spectrum of Am(V) is readily observed, little changed from its appearance in acid solution.

(2) **Reduction of Am(VI) by Water.**—Under certain conditions, Am(VI) is reduced much more rapidly than can be explained by radiolytic reduction. In particular, reduction of Am(VI) to Am(V) by water is observed: (a) at low CO_3^{-2} or HCO_3^- to Am(VI) ratios [*e.g.*, 40% reduction occurs in 1 hr. at 25° in 0.02 *M* Na_2CO_3, 0.0067 *M* Am(VI)]; and (b) at high Na_2CO_3 concentrations and high temperatures [*e.g.*, in 2 *M* Na_2CO_3, 0.0005 *M* Am(VI) at 90°]. At room temperature, no indication of reduction by water is observed at high $NaHCO_3$ or Na_2CO_3 concentrations regardless of the Am(VI) concentration.

(3) **Behavior of Am(VI) toward Reducing Agents.**—Although Br^- or Cl^- rapidly reduces Am(VI) in acid solution, no reduction of Am(VI) occurs even at 90° in 0.1 *M* $NaHCO_3$ solutions made 1 *M* in NaCl or NaBr. However, Am(VI) in 0.1 *M* $NaHCO_3$ is reduced at room temperature by NaI, N_2H_4, NH_2OH, H_2O_2, $NaNO_2$, NH_4SCN, NaCN, and $Na_2C_2O_4$.

(4) **Anion Exchange Absorption.**—Am(VI) in 0.1 *M* $NaHCO_3$ is readily absorbed by a strong base anion exchanger such as Dowex 1 in the carbonate form. The resin assumes the intense red-brown color characteristic of the complex in solution. The bright green complex of Pu(VI) in carbonate solution is similarly absorbable.

Preparation of Solid Americyl(VI) Carbonates.—Red-brown barium americyl(VI) carbonate precipitates upon addition of $Ba(NO_3)_2$ to Am(VI) carbonate solutions. Calcium americyl(VI) carbonate may be prepared similarly, but the corresponding magnesium salt is appreciably more soluble.

A crystalline sodium americyl(VI) carbonate is formed rapidly upon addition of 1 ml. of saturated $Na_2CO_3{\cdot}NaHCO_3$ to 0.2 mmole of solid sodium americyl(VI) acetate. The supernatant solution is deeply colored. The same salt (as confirmed by X-ray powder pattern) is obtained by adding methanol to a solution of Am(VI) in 0.1 *M* $NaHCO_3$. From the preparation and from qualitative chemical behavior, this salt is known to contain sodium ions, Am(VI), and carbonate or bicarbonate ions. It is not, however, isostructural with the known $Na_4UO_2(CO_3)_3$, which is the uranyl compound resulting from analogous conditions of preparation.

Other preparations of sodium americyl(VI) carbonates have been carried out by O_3 oxidation of $Am(OH)_3$ slurries in the presence of about 1 to 8 moles of $NaHCO_3$ per mole of Am(III). Solid sodium americyl(VI) carbonates were obtained by evaporation of the resulting solutions in a stream of O_3. Samples prepared in this fashion have been used for study of their infrared spectra.

Infrared Spectra of Sodium Americyl(VI) Carbonates.—The infrared spectra of samples prepared as described in the preceding paragraph were obtained with a Perkin-Elmer Model 112 recording spectrophotometer using a rock salt prism. In the carbonate (C–O) stretching region, absorption attributable to complexed carbonate or bicarbonate is found.

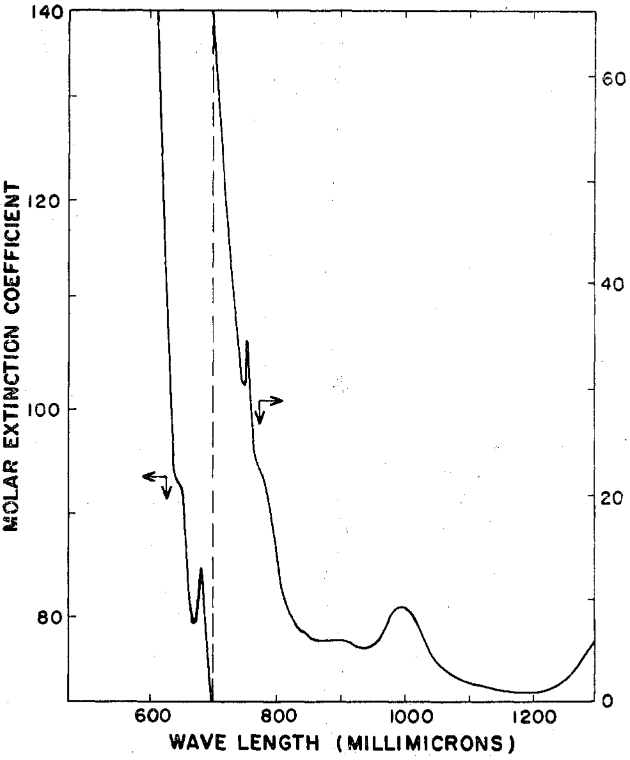

Fig. 1.—Absorption spectrum of Am(VI) in 0.1 *M* Na_2CO_3.

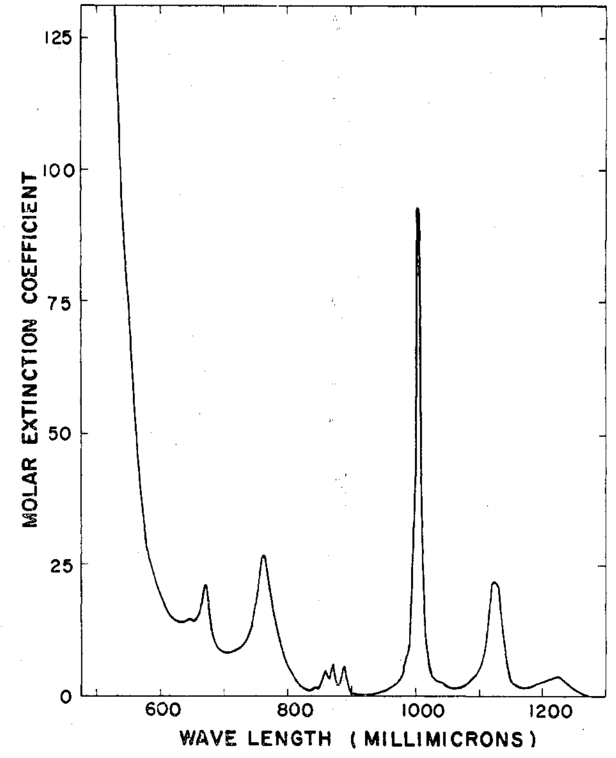

Fig. 2.—Absorption spectrum of Am(VI) in 0.1 *M* $Na_4P_2O_7$.

Two absorption bands associated with Am(VI)-containing species appear initially in all samples and disappear with time. The disappearance may be attributed to radiolytic reduction of the Am^{241}(VI). The influence of the initial $NaHCO_3$/Am mole ratio upon the observed frequency of these bands is shown in Table I. It appears that at all $NaHCO_3$/Am ratios above 2, a single species predominates.

TABLE I
INFRARED SPECTRA OF SODIUM AMERICYL(VI) CARBONATES

$NaHCO_3$/Am	ν_a, cm.$^{-1}$	ν_b, cm.$^{-1}$
7.8	897 s[a]	850 m
5.2	897 s	850 m
3.9	898 s	851 m
2.6	898 s	851 m
2.0	900 m	851 m
1.2	888 m	847 w
0.8	917 w, 900 w	

[a] s, strong; m, medium; w, weak.

The strong absorption at about 898 cm.$^{-1}$ is assigned to the O–Am–O asymmetric stretching frequency of Am(VI); this frequency appears at 914 cm.$^{-1}$ in sodium americyl(VI) acetate. The somewhat weaker absorption at about 850 cm.$^{-1}$ probably corresponds to a frequency of carbonate complexed with Am(VI), though it may be the symmetric stretching frequency of O–Am–O arising because the complex is not symmetrical in the solid state.

Preparation of Am(V) Free from Am(III).—The preparation of Am(V) by oxidation of Am(III) dissolved in alkali carbonate solution gives a product contaminated with several per cent Am(III). Such contamination is avoided through intermediate preparation of Am(VI) in 2 *M* Na_2CO_3.

A neutral or barely acid solution of Am(III) is added dropwise with vigorous stirring to 2 *M* Na_2CO_3. Any insoluble residue observed at this point is removed by centrifugation and washed free of americium with additional carbonate solution. The resulting Am(III) solution is oxidized to Am(VI) by bubbling 5% O_3 through the solution for 1 hr. at room temperature. Sodium americyl(V) carbonate then is precipitated by heating the Am(VI) solution for 30–60 min. at 90°. The spectra of solutions obtained by dissolution of the Am(V) product in dilute acid show no Am(III) or Am(VI).

Separation of Americium and Curium.—Curium(III) hydroxide, like americium(III) hydroxide, is insoluble in dilute $NaHCO_3$. Unlike americium, curium is not oxidized by O_3 or $Na_2S_2O_8$ under conditions which yield a soluble Am(VI) complex in $NaHCO_3$. These properties permit the separation of americium and curium. The process has the advantage that both elements are in a medium in which recovery and further handling is easy.

In several experiments involving 10 to 25 mg. of Am^{243} and Cm^{244} it was found that americium is oxidized to Am(VI) in dilute $NaHCO_3$ at 90° by O_3. The americium extracted contains less than 0.1 wt. % Cm^{244}. However, starting with Am^{243}/Cm^{244} weight ratios of 2:1, the curium product typically contains 5–10 wt. % Am^{243} after three cycles of oxidation. To remove the last trace of Am^{243} from the curium, it was found necessary to oxidize using peroxydisulfate in dilute acid *before* addition of $NaHCO_3$. Under the conditions described below, Am^{243} is reduced from an original 200 wt. % of the Cm^{244} to 0.1 wt. %.

(1) Initially, a slurry of the mixed hydroxides in 0.2 *M* $NaHCO_3$ is treated with O_3 at 90°. The americium-rich supernatant liquid is removed after 1 hr. For the second cycle, the curium-rich precipitate is dissolved in dilute acid, reprecipitated with NH_3, slurried again in 0.2 *M* $NaHCO_3$, and treated with O_3.

(2) After three such cycles the mixed hydroxides are dissolved in 0.5 *M* $Na_2S_2O_8$ and a minimum of acid and heated to 90° for 30 min. to oxidize Am(III) to Am(VI).[8] Curium is precipitated by addition of hot 0.5 *M* $NaHCO_3$–0.5 *M* $Na_2S_2O_8$. The precipitate is digested twice for 30 min. with fresh portions of hot 0.5 *M* $NaHCO_3$–0.5 *M* $Na_2S_2O_8$, which removes the last traces of americium.

Because of the reducing effects of the high level of Cm^{244} activity (1.85×10^{11} α/min./mg.) the supernatant solutions must be removed quickly and, in the case of solutions containing $Na_2S_2O_8$, must be maintained at 90°. Otherwise, the color of the Am(VI) complex fades perceptibly within a few minutes.

Discussion

Stability of Am(VI) in Carbonate Solution.—Am(VI) is a strong oxidizing agent. The potential of the Am(V)–Am(VI) couple (−1.6 volts) is comparable to the potentials of the MnO_2–MnO_4^- or Ce(III)–Ce(IV) couples.[9] Although Am(VI) is thermodynamically unstable with respect to reduction by water, it falls within the region of stability for oxidizing agents given by Latimer for acidities greater than about 0.01 *M*. At higher pH, oxidation of water may be expected unless the americyl(VI) ion is stabilized relative to the americyl(V) ion, for example, through complex formation.

Am(VI) is strongly stabilized in the presence of carbonate or bicarbonate ions. In such solutions Am(V) forms rather insoluble double salts. The balance between these two effects determines the stability of Am(VI) under various experimental conditions. Thus, in the presence of potassium ion, Am(VI) is readily reduced by water with precipitation of potassium americyl(V) carbonate; oxidation of Am(III) in $KHCO_3$ yields only Am(V) and fails to produce Am(VI). Under these circumstances, the low solubility of potassium americyl(V) carbonate is controlling. Sodium americyl(V) carbonate is more soluble. As a result, Am(VI) is stable in 0.1 to 1 *M* $NaHCO_3$ and is formed readily in these media by oxidation of Am(III) or Am(V). Am(VI) is similarly stable in dilute Na_2CO_3 solutions. However, at low carbonate/Am(VI) ratios or at high Na_2CO_3 concentrations and high temperatures the rate of reduction by water again becomes appreciable.

On the basis of the experiments with various oxidizing and reducing agents, the potential of the Am(V)–Am(VI) couple in 0.1 *M* $NaHCO_3$ is estimated to be about −1 volt.

Nature of Complex Species in the Am(VI)–Carbonate System.—The sharp absorption ordinarily observed in the solution spectra of actinide ions may be attributed to transitions involving shielded 5f electrons. Such transitions are typically insensitive to formation of complex ions and, in fact, the spectrum of Am(VI) is not greatly changed by formation of complexes with nitrate, sulfate, fluoride, or pyrophosphate. The spectra in carbonate and bicarbonate solutions exhibit a profound change which implies a modification of the immediate environment about the Am(VI), different in character from that occurring with pyrophosphate, fluoride, etc.

The observations of the spectra of Am(VI) in the presence of mixtures of Na_2CO_3 with other complexing agents indicate that hydroxide ion is bound by Am(VI) more tightly than carbonate, that the formation con-

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[8] Oxidation of Am(III) to Am(VI) in the presence of Cm(III) under similar conditions is described by S. E. Stephanou and R. A. Penneman, *J. Am. Chem. Soc.*, **74**, 3701 (1952).

[9] W. M. Latimer, "Oxidation Potentials," Second Ed., Prentice-Hall, New York, N. Y., 1952.

stants for the complex species formed in 0.1 *M* Na_2CO_3 and in 0.1 *M* $Na_4P_2O_7$ are roughly equal, and that carbonate is bound much more tightly than sulfate, fluoride, bromide, and chloride.

U(VI) forms well defined $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$ species in solution with over-all stability constants, according to the work of Babko and Kodenskaya,[10] of 3.7×10^{15} and 5×10^{20}, respectively. The complexes of Am(VI) are similar to those of U(VI) in being readily precipitated by barium and calcium ions and absorbed by anion exchange resins in the carbonate form. The infrared spectra of solid sodium americyl(VI) carbonates establish the persistence of the O–Am(VI)–O group, and the presence of complexed carbonate or bicarbonate. However, under conditions which yield $Na_4UO_2(CO_3)_3$, an isostructural Am(VI) carbonate is not obtained. This result, together with the pronounced change in the Am(VI) spectrum in carbonate, suggests that Am(VI) exhibits a greater tendency toward hydrolysis or polymerization than does U(VI) in the presence of carbonate ion.

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Covalency of Metal–Ligand Bonds in Hexahaloselenates(IV) Studied by the Pure Quadrupole Resonance of Halogens

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The pure quadrupole resonance of halogens in some hexahaloselenates(IV) was observed at various temperatures. These complexes show a single resonance line, indicating that all halogen atoms in each compound are crystallographically equivalent except for potassium hexabromoselenate(IV) at temperatures below −33°. For this compound, three transition points are located between room and Dry Ice temperatures. The ionic character of selenium–halogen bonds and the net charge on a selenium atom were evaluated by means of the Townes–Dailey procedure. The covalent character plotted against the electronegativity difference between selenium and halogens practically coincides with the corresponding plot of hexahalotellurates(IV), yielding a single straight line. The net charge on the selenium atom is approximately equal to a unit positive charge, in agreement with the theoretical prediction based on the electronic configuration of a selenium atom.

Introduction

In discussing the nature of metal–ligand bonds in metal complexes, often use is made of rather vague terms such as covalent character, ionic character, and the hybrid of these in order to explain various properties of the complex compounds. However, in order to establish these concepts in a quantitative manner and to express the transition from ideal covalent bonds to pure ionic bonds, one must define the extent of covalent character by resorting to some experimental parameters that are characteristic of metal–ligand bonds and are measurable accurately. Pure quadrupole resonance frequencies can afford to give the necessary information. According to this definition, the covalent character of a metal–ligand bond is $1 - i$, where the ionic character i is given by the number of electrons belonging to the ligand atom in a metal complex minus the number of electrons in a free ligand atom.

We have observed the pure quadrupole resonance frequencies of halogens in a number of hexahalo complexes and discussed the covalent character of metal–ligand bonds in these complexes.[1–4] Conclusions were derived that for a given central atom the covalent character decreases with increasing electronegativity of halogens and that the electronic configuration of the central atom plays a major role in determining the covalent character of metal–ligand bonds and in varying the net charge on central atoms to a considerable extent. In order to gain some insight into this problem, it is of interest to study hexahaloselenates(IV) and compare the results with those of hexahalotellurates(IV) already studied, because selenium and tellurium have the same outer electronic configuration but differ in their electronegativities by as much as 0.3.[5]

Experimental

Apparatus.—Super-regenerative spectrometers already described[1] were used for the determination of the pure quadrupole resonance of halogens.

Materials.—A commercial preparation of selenous acid, H_2SeO_3, was dissolved in concentrated hydrochloric acid. On passing hydrogen chloride through the solution, to which potassium chloride was added in advance, potassium hexachloroselenate(IV) precipitated.[6] The precipitates were washed with concentrated hydrochloric acid and dried in a stream of hydrogen

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