A new mechanism is proposed in this paper to overcome these difficulties. As can be seen below, the rate-determining step is assumed to be the reaction between $FeOH^+$ and O_2OH^-, the latter species being the intermediate to form the "peroxide-like oxygen" as can be seen in eq 3.

$$\begin{aligned} Fe^{2+} + OH^- &\rightleftharpoons FeOH^+, \quad K_{FeOH^+} = \frac{[FeOH^+]}{[Fe^{2+}][OH^-]} \\ O_2 + OH^- &\rightleftharpoons O_2OH^-, \quad K_{O_2OH^-} = \frac{[O_2OH^-]}{[O_2][OH^-]} \end{aligned} \qquad (6)$$

$$FeOH^+ + O_2OH^- \xrightarrow{\text{slow}} Fe(OH)_2^+ + O_2^-, \; O_2^- + H^+ \rightleftharpoons HO_2 \qquad (7)$$

The rate equation will be

$$\begin{aligned} -\frac{d[Fe(II)]}{dt} &= 4k[FeOH^+][O_2OH^-] \\ &= 4kK_{FeOH^+}K_{O_2OH^-}\frac{[Fe(II)]}{1 + K_{FeOH^+}[OH^-]} \times \frac{[O_2]_{total}}{1 + K_{O_2OH^-}[OH^-]}[OH^-]^2 \end{aligned} \qquad (8)$$

where $[Fe(II)] = [Fe^{2+}] + [FeOH^+]$ and $[O_2]_{total} = [O_2] + [O_2OH^-]$. Calculations with $K_{FeOH^+} = 10^{4.5}$ reported by Hedström[8] indicated that, at pH's below 7.5, the term $K_{FeOH^+}[OH^-]$ in eq 8 can be neglected compared to 1.

As pointed out above, the solubility of oxygen does not increase even when the alkalinity of the solution is raised to 2 N in NaOH.[7] This means that $[O_2OH^-]$ is far less than $[O_2]$. Since $[O_2OH^-]$ is much less than $[O_2]$ at pH 14.3, *i.e.*, in 2 N NaOH solution, the value of $K_{O_2OH^-}$ should be far less than $10^{-0.3}$. It is also seen that, at pH's below 7.5, $K_{O_2OH^-}[OH^-]$ in eq 8 is negligible compared to 1, and $[O_2]_{total}$ can be replaced by $[O_2]$. In this way, eq 8 is simplified to

$$-\frac{d[Fe(II)]}{dt} = 4kK_{FeOH^+}K_{O_2OH^-}[Fe(II)][O_2][OH^-]^2 \qquad (9)$$

By comparing eq 1 with 9, we can put

$$k_0 = 4kK_{FeOH^+}K_{O_2OH^-} = 5.7 \times 10^{13} \qquad (10)$$

The value of k must be smaller than the rate constant 1.4×10^{11} for the reaction between H^+ and OH^-. Therefore, the smallest possible value of $K_{O_2OH^-}$ is $10^{-2.5}$. Thus, if the proposed mechanism is valid, the value of $K_{O_2OH^-}$ should lie in the range

$$10^{-2.5} < K_{O_2OH^-} < 10^{-0.3} \qquad (11)$$

from which it will be seen that the value of the specific rate constant k lies in the range

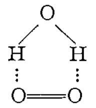
$$4.6 \times 10^9 < k < 1.4 \times 10^{11} \qquad (12)$$

Such a large value of k suggests that the reaction between $FeOH^+$ and O_2OH^- is most likely diffusion controlled and predicts the activation energy to be very small. Stumm and Lee[2] estimated an apparent activation energy to be 23 kcal/mol from the temperature dependence of the overall rate constant k_0 in eq 1. However, since k_0 depends on k, K_{FeOH^+}, and $K_{O_2OH^+}$ as will be seen in eq 10 the apparent activation energy is the sum of three terms

$$E_{app} = E_a + \Delta H°_{FeOH^+} + \Delta H°_{O_2OH^-}$$

where E_a is the activation energy of the reaction between $FeOH^+$ and O_2OH^- and $\Delta H°_{FeOH^+}$ and $\Delta H°_{O_2OH^-}$ are the enthalpies of the formation reaction of $FeOH^+$ and O_2OH^-, respectively.

Heidt and Johnson[9] obtained some evidence that the oxygen molecules dissolved in water are hydrated to form $OH_2 \cdots O{=}O \cdots H_2O$ and/or



Then it is reasonable to assume that the water molecules coordinated to oxygen can dissociate in the same sense as in the hydrolysis of metal ions. The forms of oxygen ions O_2OH^- and O_3^{2-} will be equivalent to the first-step and the second-step dissociated forms of hydrated oxygen molecule described above.

The values of $\Delta H°_{FeOH^+}$ and $\Delta H°_{O_2OH^-}$ will be about 10 kcal/mol because the enthalpies of the dissociation reactions of these hydrated species are expected to be about the same as that of the neutralization of weak acid with base. Hence the value of E_a is 3 kcal/mol, consistent with the above assumption that the rate-determining process is controlled by the diffusion of $FeOH^+$ and O_2OH^-.

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[8] B. O. A. Hedström, *Arkiv Kemi*, **5**, 457 (1953).

[9] J. Heidt and A. M. Johnson, *J. Am. Chem. Soc.*, **79**, 5587 (1957).

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Plutonium Species in Propane-1,2-diol Carbonate Solution. Preparation of a Multivalent Plutonium Compound

BY J. M. CLEVELAND, G. H. BRYAN, AND W. G. EGGERMAN

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Aside from brief spectrophotometric studies in dimethylformamide, dimethyl sulfoxide, and ethanol[1] and a more thorough study in anhydrous acetic acid,[2] the chemistry of plutonium in nonaqueous solvents has been neglected, despite the potential advantages resulting from the absence of strong solvent coordination and hydrolysis. This paper describes an investigation using propane-1,2-diol carbonate (PDC), whose high dielectric constant of 69,[3] convenient liquid range, and chemical stability make it a promising choice for a nonaqueous solvent. The plutonium–chloride system was selected for study because of the ready

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[1] A. Ekstrom, M. S. Farrell, and J. J. Lawrence, *J. Inorg. Nucl. Chem.*, **30**, 660 (1968).

[2] M. Alie, Q. C. Johnson, H. D. Cowan, and J. F. Lemons, *ibid.*, **29**, 2327 (1967).

[3] "Propylene Carbonate," Technical Bulletin, Jefferson Chemical Co., Houston, Texas, 1956.

availability of salts containing Pu(III) and Pu(IV)—*i.e.*, $PuCl_3$ and Cs_2PuCl_6, respectively—which presumably could be used for solution preparation.

Experimental Part

Propane-1,2-diol carbonate was obtained from Jefferson Chemical Co. and purified by distillation at a pressure of 3 Torr using a still of the type described by Schlafer and Schaffernicht.[4] The purified solvent, containing less than 10 ppm of water, was stored under argon in tightly stoppered brown bottles. Plutonium chloride was prepared by the reaction of PuO_2 (made by calcination of plutonium peroxide) with CCl_4 vapor in a Vycor tube at 650°. Analysis indicated the material contained 30.67% Cl (theoretical value for anhydrous $PuCl_3$, 30.79%). The salt Cs_2PuCl_6 was prepared by addition of CsCl solution to a solution of Pu(IV) in concentrated HCl, followed by filtration and drying of the resultant precipitate.[5]

The solubility of $PuCl_3$ in propane-1,2-diol carbonate was determined by the mechanical agitation in a constant-temperature bath at 25.0 ± 0.5° of tightly sealed volumetric flasks containing solvent and an excess of the salt. To exclude air and moisture, the flasks were purged with argon before and after filling, and the stoppers were sealed with paraffin. Attainment of equilibrium was demonstrated by the close analytical agreement between samples agitated for 6 and for 13 days. The solubility of Cs_2PuCl_6 was measured in a similar manner. In both cases the dissolved salt content was determined by analysis for chloride. The solubility of chlorine in propane-1,2-diol carbonate was measured by passing the gas through the solvent at room temperature (23 ± 1°) for 120 min and determining the chlorine content of the resulting solution by iodometric titration.

Solid samples were analyzed for chloride by dissolution in water (comparison runs using water and dilute acid gave the same results, indicating that plutonium hydrolysis did not affect the analysis) followed by potentiometric titration with $AgNO_3$ using a silver indicator electrode and a calomel reference electrode. Analysis of solid compounds for plutonium involved destruction of the organic material, followed by redox titration with ceric ion, with photometric detection of the end point using ferroin indicator.[6] Carbon was determined by combustion in a Coleman carbon–hydrogen analyzer, with the product CO_2 being absorbed on an Ascarite column and weighed.

All infrared spectra were determined on a Perkin-Elmer 521 spectrophotometer, with solids being run in KBr pellets. Visible and near-infrared spectra were measured on a Cary Model 14 recording spectrophotometer. Solutions were scanned using a propane-1,2-diol carbonate blank, while solids were run as a mull in fluorocarbon grease using a $CaCO_3$ mull as blank to balance the light scattering in the sample.

Results and Discussion

The solubility of $PuCl_3$ in propane-1,2-diol carbonate at 25.0 ± 0.5° is 0.0134 ± 0.0005 *M*. This value is the mean of 10 different determinations, and the error cited in this and the other solubility values below is the standard deviation. The mean of 16 determinations of the solubility of Cs_2PuCl_6 in this solvent at 25.0 ± 0.5° is 0.0603 ± 0.0011 *M*. The average solubility of chlorine in PDC from six separate measurements was 0.613 ± 0.004 *M* at 23 ± 1° and a pressure of approximately 610 Torr.

Because of the low solubility of $PuCl_3$ and Cs_2PuCl_6 in this solvent, plutonium solutions were prepared by direct dissolution of the metal in chlorine-saturated propane-1,2-diol carbonate, and in this manner solutions containing up to 0.6 *M* plutonium were routinely obtained. Plutonium was the only cation present in the resulting solutions, since the solvent has no acid properties and furthermore is attacked only slowly by chlorine, thus eliminating the possibility of producing cationic species by solvent decomposition.

The visible spectrum of this solution is shown in Figure 1. Comparison with the spectra of Cs_2PuCl_6 and $PuCl_3$ indicates that the solution contains primarily Pu^{3+} and $PuCl_6^{2-}$ with perhaps a minor concentration of a lower plutonium(IV)–chloro complex. The molar absorptivities were determined for the principal peaks of Pu^{3+} (26 at 564, 19 at 595, 11 at 669, 11 at 796, 12 at 899, 12 at 1104 nm) and $PuCl_6^{2-}$ (21 at 692, 14 at 835, 11 at 845, 5 at 905, 6 at 1122 nm) in PDC and from these the relative concentrations of Pu^{3+} and $PuCl_6^{2-}$ in the solution were calculated and are given in Table I. The calculated percentages of the two species, based on the charge-balance requirement, are 40 and 60, respectively. Thus complete oxidation of the Pu^{3+} to $PuCl_6^{2-}$ was apparently prevented by the absence of any other cation to maintain charge balance, and this conclusion was supported by the observation that passage of chlorine through the solution for prolonged periods did not alter the relative amounts of $PuCl_6^{2-}$ and Pu^{3+}.

TABLE I

COMPOSITIONS OF SOLUTIONS OF PLUTONIUM IN CHLORINE-SATURATED PROPANE-1,2-DIOL CARBONATE

	%	
Soln	Pu^{3+}	$PuCl_6^{2-}$
A	43	57
B	45	55
C	42	58
D	38	62
E	39	61
F	42	58
G	42	58

Addition of benzene to the solution caused precipitation of a green compound, which was washed several times with benzene and dried under vacuum to produce a free-flowing powder. Comparison of the visible spectrum of a mull of this compound with that of $PuCl_3$ and $PuCl_6^{2-}$ indicates that it is a composite of the two, with only minor shifts in peaks. The spectrum of this compound is very similar to that of the solution before precipitation, as shown in Figure 1, indicating that the compound precipitated contained the same species present in the solution, and the infrared spectrum indicated that propane-1,2-diol carbonate was the only organic species present. Based on these observations and the elemental analysis data shown in Table II it is concluded that the compound is $Pu^{III}{}_2(Pu^{IV}Cl_6)_3 \cdot n\mathrm{PDC}$, where *n* is probably 14. This is the first known preparation of a discrete stoichiometric compound containing plutonium in two different oxidation states.

Addition of benzene to a propane-1,2-diol carbonate solution of Cs_2PuCl_6 caused the compound to precipitate,

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(4) H. L. Schlafer and W. Schaffernicht, *Angew. Chem.*, **72**, 618 (1960).

(5) F. J. Miner, R. P. DeGrazio, and J. T. Byrne, *Anal. Chem.*, **35**, 1218 (1963).

(6) C. E. Caldwell, L. F. Grill, R. G. Kurtz, F. J. Miner, and N. E. Moody, *ibid.*, **34**, 346 (1962).

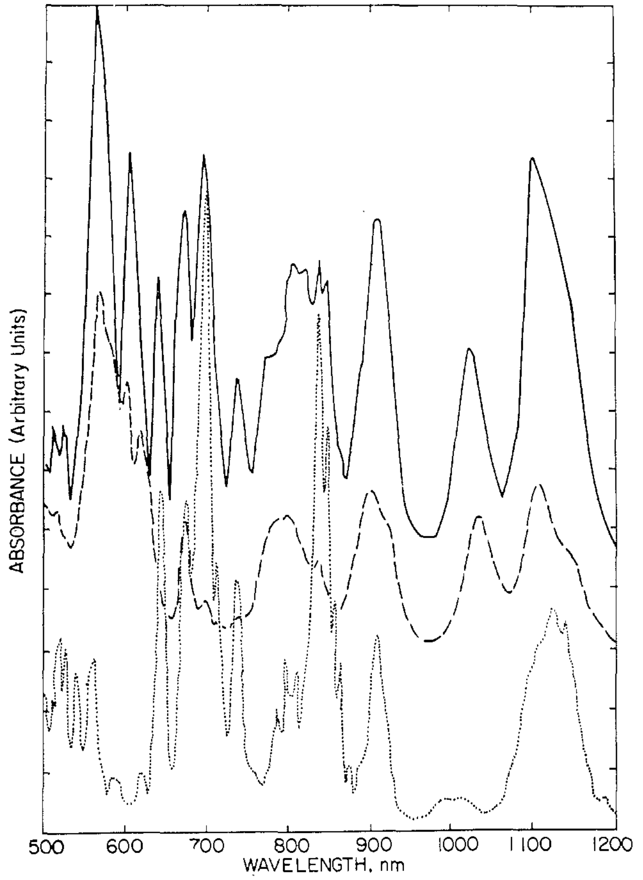

Figure 1.—Absorption spectra of plutonium species in propane-1,2-diol carbonate solution: ———, plutonium dissolved in chlorine-saturated propane-1,2-diol carbonate; – – –, $PuCl_3$ in propane-1,2-diol carbonate; · · · · ·, Cs_2PuCl_6 in propane-1,2-diol carbonate.

TABLE II

COMPOSITION OF PLUTONIUM–CHLORIDE PRECIPITATES

Prepn	Pu (%)	Cl (%)	C (%)
1	37.5	18.6	21.2
2	37.4	18.8	20.5
3	34.8	18.7	20.7
4	35.2	18.6	20.7
5	36.9	19.0	. . .
	Calcd		
$Pu_2(PuCl_6)_3 \cdot 12PDC$	39.1	20.9	18.8
$Pu_2(PuCl_6)_3 \cdot 14PDC$	36.6	19.6	20.6
$Pu_2(PuCl_6)_3 \cdot 16PDC$	34.5	18.4	22.2

and after drying, analysis indicated that it did not contain carbon. It was therefore concluded that the $PuCl_6^{2-}$ anion does not contain any molecules of solvation and that all the solvent molecules in $Pu_2(PuCl_6)_3 \cdot n$PDC were coordinated to the Pu^{3+} ions.

Oxidation of Pu(III) to Pu(IV) is favored by stabilization of the latter as the hexachloro complex and is quantitative under favorable conditions. Thus, addition of a solution of $(C_2H_5)_4NCl$ in propane-1,2-diol carbonate to a solution of Pu^{3+} and $PuCl_6^{2-}$ in the same solvent (saturated with chlorine) caused all the Pu^{3+} to be oxidized to hexachloroplutonate(IV) by dissolved chlorine. In this case $(C_2H_5)_4NCl$ supplied chloride anions to complex Pu(IV) and $(C_2H_5)_4N^+$ cations necessary for charge balance. However, the presence of cations is not in itself sufficient to permit the oxidation; addition of $(C_2H_5)_4NClO_4$ solution to another sample of the original solution did not alter the relative percentages of Pu^{3+} and $PuCl_6^{2-}$. In this case insufficient chloride ions were present to complex the Pu(IV).

The mechanism of dissolution of plutonium in chlorine-saturated propane-1,2-diol carbonate is not well understood. Initially it was thought likely that the metal was dissolved to form Pu(III), which was then oxidized to $PuCl_6^{2-}$, but this explanation was not supported by the observation that $PuCl_3$ is relatively insoluble in chlorine-saturated propane-1,2-diol carbonate. Nevertheless, the bluish appearance of the metal when removed from the solvent suggests that dissolution does proceed through the formation of Pu(III).

In summary, solutions of plutonium in reasonable concentrations in propane-1,2-diol carbonate may be prepared by dissolution of the metal in chlorine-saturated solvent. The resulting solution contains Pu(III), $PuCl_6^{2-}$, and possibly a minor concentration of lower anionic complexes of Pu(IV) as the only ionic species. Addition of benzene to the solution causes precipitation of a compound containing only these ions, namely, $[Pu^{III}(PDC)_7]_2(Pu^{IV}Cl_6)_3$. Future plans involve investigation of the plutonium–bromide and plutonium–iodide systems in propane-1,2-diol carbonate.

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The Structure of Cobalt(II) Complexes with Quadridentate Schiff Bases in Solution and the Solid State

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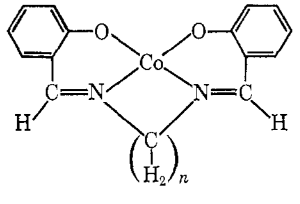
In a recent publication[2] the synthesis was described of a series of cobalt(II) complexes with N,N′-bis(salicylidene)polymethylenediamine ligands



The complexes with n ranging from 3 to 6 were said to

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(1) Weizmann Institute of Science, Rehovoth, Israel. Work performed while on leave of absence.

(2) M. Hariharan and F. L. Urbach, *Inorg. Chem.*, **8**, 556 (1969).