Inorg. Chem. **2006**, *45*, 8483–8485

Inorganic Chemistry

Communication

The Structure and Synthesis of Plutonium(III) Chlorides from Aqueous Solution

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Received June 2, 2006

The preparation and structure of three trivalent plutonium chloride compounds from aqueous solution is reported. Two of the three are plutonium tetraaquatetrachloro complexes exhibiting a cis and a trans arrangement of Cl about the Pu. The identification of the coordination number of 4 with respect to Cl and the isomerism are both unprecedented in actinide solution chemistry. The third complex is a hexaaquadichloro complex of Pu(III), predicted by available thermodynamic data.

The anhydrous trichloride salts of the lanthanides and actinides prepared through high-temperature and/or solid-state methods are well documented.[1] Several studies and structures are available for the complex salts of the lanthanides and actinides spanning dichloro through hexachloro species with coordination numbers of 6−9 synthesized by either high-temperature or solution methods.[2−14]

Noticeably absent are structures of hydrated plutonium(III) chlorides. Studies on the complexation of Pu(III) by chloride in aqueous solution have proven to be inconclusive and contradictory. A handful of X-ray spectroscopy experiments provide little or no evidence to support inner-sphere coordination of chloride to Pu(III) in aqueous solution, although such coordination is demonstrated for several lanthanides and the heavier trivalent actinide ions Am(III) and Cm(III).[15−17] The Nuclear Energy Agency thermodynamic review provides stability constants for mono- and dichloroplutonium(III) complexes based on measurements using ion-exchange and solvent extraction recommending only $\log \beta^0(\mathrm{PuCl}^{2+}) = 1.2 \pm 0.2$ and provides a constant $\log \beta(\mathrm{PuCl_2}^{+}, 1{-}13\ \mathrm{M\ LiCl}) = -5.00 \pm 0.06$.[18] The referenced experiments employing extended X-ray absorption fine structure (EXAFS) could not substantiate these results or any inner-sphere chloride coordination in Pu(III) even at 12 M chloride concentrations and suggest that in aqueous solution the chlorine is not directly bound to Pu(III).[15,16]

Not surprisingly, in consideration of the magnitude of the measured stability constants for the known chloride complexes, little is known about the structures of chloride compounds of Pu(III) from aqueous solution. A handful of syntheses report the preparation of complex trihalide salts from organic solution as useful starting materials for actinide organometallics and spectroscopic studies,[19−21] and there is one report of a $\mathrm{Cs_3PuCl_6{\cdot}2H_2O}$ complex of unknown structure.[22]

Several attempts to prepare the trivalent chlorides from aqueous solution have been reported but resulted only in the

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10.1021/ic060979a CCC: $33.50

Table 1. Summary of Crystallographic and Structural Details[25]

	cis-$Cs[PuCl_4(H_2O)_4]$	*trans*-$Cs_5[PuCl_4(H_2O)_4]Cl_4{\cdot}2H_2O$	$(Et_4N)[PuCl_2(H_2O)_6]Cl_2{\cdot}2H_2O$
	Space Group and Cell Parameters		
	$P2_12_12$ (No. 18)	$P2_1$ (No. 4)	$P1$ (No. 1)
$T = -100$ °C	$a = 7.091$ Å, $b = 11.233$ Å, $c = 6.785$ Å	$a = 9.158$ Å, $b = 9.883$ Å, $c = 14.243$ Å	$a = 8.631$ Å, $b = 11.06$ Å, $c = 12.111$ Å
$\lambda = 0.710\ 73$ Å	$\alpha = \beta = \gamma = 90°$	$\beta = 104.52°$	$\alpha = 88.31°$, $\beta = 89.69°$, $\gamma = 74.60°$
Mo Kα	$V = 540.3$ Å^3, $Z = 2$	$V = 1247.96$ Å^3, $Z = 2$	$V = 1114.24$ Å^3, $Z = 2$
	$D_{calc} = 3.63$ g cm^{-3}, $\mu = 10.370$ cm^{-1}	$D_{calc} = 3.46$ g cm^{-3}, $\mu = 10.693$ cm^{-1}	$D_{calc} = 1.912$ g cm^{-3}, $\mu = 3.463$ cm^{-1}
R, wR	0.0250, 0.0444	0.0217, 0.0543	0.0619, 0.0763
	Bond Distances, Å		
	Pu−O1 = 2.506(3)	Pu−O1 = 2.491(3)	Pu−O1 = 2.498(5)
	Pu−O2 = 2.521(3)	Pu−O2 = 2.515(3)	Pu−O2 = 2.485(4)
	Pu−Cl1 = 2.838(1)	Pu−O3 = 2.538(3)	Pu−O3 = 2.475(4)
	Pu−Cl2 = 2.820(1)	Pu−O4 = 2.567(3)	Pu−O4 = 2.448(4)
		Pu−Cl1 = 2.808(1)	Pu−O5 = 2.479(4)
		Pu−Cl2 = 2.812(1)	Pu−O6 = 2.476(5)
		Pu−Cl3 = 2.777(1)	Pu−Cl1 = 2.804(2)
		Pu−Cl4 = 2.783(1)	Pu−Cl2 = 2.811(2)
	Average Bond Angles, deg		
	O−Pu−O = 72.75, 136.92	O−Pu−O = 69.17, 130.60	O−Pu−O = 71.91−146.37
	Cl−Pu−Cl = 81.93, 154.22	Cl−Pu−Cl = 94.74, 146.55	Cl−Pu−Cl = 94.17

formation of the tetravalent plutonium chloride salts.[23] One of the challenges in preparing Pu(III) compounds from acidic aqueous solution is holding Pu(III) in the reduced state and avoiding its oxidation to Pu(IV) or higher oxidation states in the ambient atmosphere in the presence of even weakly coordinating ligands (i.e., chloride) for time periods required for crystallization. We have overcome this problem by the addition of large excesses of powerful reducing agents to the system, hydroxylamine or hydrogen peroxide, thus enabling the crystallization of trivalent plutonium chlorides from aqueous solution.

From acidic solution containing either CsCl or KCl, two ^{242}Pu tetraaquatetrachloro compounds of the form $[PuCl_4(H_2O)_4]^{-1}$ exhibiting a cis and a trans arrangement of chlorine about the Pu atom have been crystallized and structurally characterized by diffraction methods. Similarly, from acidic solution, $(Et_4N)[PuCl_2(H_2O)_6]Cl_2{\cdot}2H_2O$ has been synthesized and its structure determined by diffraction methods. The tetraaquatetrachloro compounds represent an unprecedented coordination of four Cl atoms about the Pu(III) center as well as cis and trans isomerism. These three new structures supplement the reported structures of the anhydrous plutonium tri-, penta-, and hexachloro compounds synthesized through high-temperature and solid-state methods.

cis-$PuCl_4(H_2O)_4^{-1}$ was synthesized by the precipitation of ^{242}Pu(IV) as the salt Cs_2PuCl_6 using literature methods[24] and the exposure of the dry crystals to a solution of saturated hydroxylamine hydrochloride and saturated CsCl in concentrated HCl. The yellow-orange Cs_2PuCl_6 crystals quickly took on a blue color, and the excess solution was removed from the vessel and the slurry allowed to dry in air. Simply mixing the hydroxylamine into the Cs_2PuCl_6-containing solution with subsequent evaporation produced smaller blue crystals embedded in a cake of hydroxylamine crystals. Both methods produced crystals suitable for diffraction studies, the former more reliably.

trans-$Cs_5[PuCl_4(H_2O)_4]Cl_4{\cdot}2H_2O$ was synthesized by the precipitation of ~0.05 M Pu(IV) in concentrated HCl with 2 mL of 0.25 M CsCl in concentrated HCl. To this slurry was added 1 mL of 30 wt % H_2O_2 and 1 mL of concentrated HCl. Vigorous dissolution of the Pu(IV) solid and peroxide resulted in a blue-purple solution that was transferred to a Petri dish, in which, after evaporation, a blue and yellow crystalline residue remained. The yellow compound was identified as Cs_2PuCl_6, while the blue crystals were identified as $Cs_5[PuCl_4(H_2O)_4]Cl_4{\cdot}2H_2O$.

$(Et_4N)[PuCl_2(H_2O)_6]Cl_2{\cdot}2H_2O$ was crystallized from a 1 M HCl solution formed by dilution of a 0.4 M Pu solution in concentrated HCl with 0.25 M tetraethylammonium chloride and the addition of 100 mg of hydroxylamine as a reducing agent. This compound cocrystallized with needles of hydroxylamine upon evaporation. The yields for all three syntheses were low. Crystals suitable for diffraction studies were mechanically separated from impurities under an inert oil.

The structure of *cis*-$Cs[PuCl_4(H_2O)_4]$ is presented in Figure 1a, with the crystallographic details presented in Table 1. The Pu atom is eight-coordinate, with four H_2O molecules and four Cl atoms occupying two discrete halves of the coordination sphere in a cis arrangement. The 8-fold coordination results in a distorted square antiprism with four Cl and four O atoms at each of the prism vertexes. The Pu−Cl bond distances are 2.820(1) and 2.838(1) Å, while the Pu−O distances for the coordinating water are 2.506(3) and 2.521(3) Å. The Pu−Cl bond distances in this eight-coordinate complex are intermediate to the Pu−Cl bond distances reported for the nine-coordinate $PuCl_3$ (2.894 Å)[26] and seven-coordinate K_2PuCl_5 (2.781 Å).[10] The Pu−O distances are also consistent with the Pu−O bond distances reported in the compound $[Pu(H_2O)_9][CF_3SO_3]_3$ of 2.574 and 2.476 Å[27] and earlier EXAFS studies.[15,16] The nearest charge

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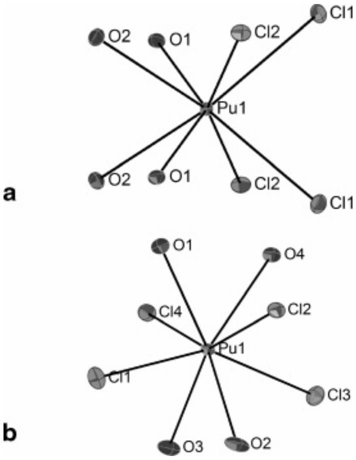

Figure 1. Thermal ellipsoid plot of (a) *cis*-$Cs[PuCl_4(H_2O)_4]$ and (b) *trans*-$Cs_5[PuCl_4(H_2O)_4]Cl_4{\cdot}2H_2O$ at 50% probability.

balancing Cs atom is 4.844 Å from the Pu atom. This cis arrangement has been previously demonstrated in La complexes isolated from aqueous solution and U complexes from organic solvents.[21,28]

The structure of the anion *trans*-$PuCl_4(H_2O)_4^-$ is shown in Figure 1b. This molecule crystallized in a complex matrix with a formula of $Cs_5[PuCl_4(H_2O)_4]Cl_4{\cdot}2H_2O$. The Pu atom is eight-coordinate, forming a distorted dodecahedron with Pu−Cl distances spanning 2.777(1)−2.812(1) Å in excellent agreement with literature values for the anyhydrous chloride salts[10,26] but slightly shorter than the Pu−Cl distances in the cis compound. The Pu−O distances for the coordinating water, 2.491(3)−2.567(3) Å, agree with previously reported values for the plutonium(III) aquo ion[27] and are identical with those found in the cis compound. While complexes of similar stoichiometry are known in the lanthanides and U,[21,28] this trans arrangement of the Cl atoms is to our best knowledge unreported.

The actinide cation in the compound $(Et_4N)[PuCl_2(H_2O)_6]Cl_2{\cdot}2H_2O$ is isostructural with the corresponding lanthanide hexaaquadichloro complexes and represents the highest chloride coordination number previously reported from thermodynamic studies in aqueous solution.[18,29] Figure 2 shows the coordination about the Pu atom, demonstrating the bicapped trigonal-prismatic arrangement of coordinating ions. The Pu−Cl [2.804(2) and 2.811(2) Å] and Pu−O [2.447(5)−2.497(5) Å] bond distances are consistent with those demonstrated in the tetrachloride complexes.

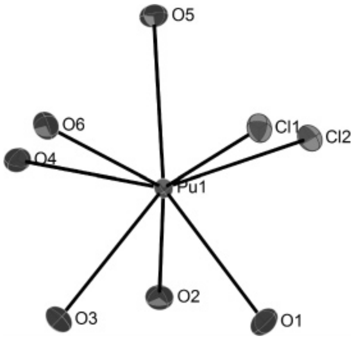

Figure 2. Thermal ellipsoid plot of $(Et_4N)[PuCl_2(H_2O)_6]Cl_2{\cdot}2H_2O$. Ellipsoids are at 50% probability.

When the cis and trans structures of the tetrachlorides are compared, the Pu−Cl bond distances are slightly elongated in the cis structure, accompanied by average Cl−Pu−Cl bond angles of approximately 82° versus nearly 95° in the trans compound. The opposite is true for the O−Pu−O bond angles, with the average O−Pu−O angle only 3.6° more acute in the trans than in the cis structure. These differences result in nearest Cl−Cl distances that are on average 0.44 Å longer in the trans structure than the cis, while the O−O distances are 0.11 Å closer. Additionally, the O−Cl distances in the trans compound are, on average, about 0.09 Å longer than those in the cis structure. Though the trans arrangement seems to be a marginally less strained structure, there are no definitively clear indications as to the stability of one conformation versus the other from the structural data, only that the entirety of the previously reported compounds have been of the *cis*-$MCl_4(H_2O)_4^-$ (M = Ln, U) type.

The three structures reported here represent the first trivalent actinide tetrachloride and dichloride complexes prepared from aqueous solution. The isolation of the isomeric pair of cis and trans tetraaquatetrachloro complexes is unknown in similar lanthanide structures. Previous thermodynamic studies on the complexation of Pu(III) in chloride solution suggest only the complex $PuCl_2^+$ or $PuCl^{2+}$. The dichloro complex of the thermodynamic studies was observed only under very high chloride concentrations.[17,18] The need for high salt concentrations (near evaporative dryness) to produce the three complexes reported here is consistent with the weakly complexing nature of the Cl ion to Pu(III) in solution. Though no evidence exists that tetrachloro complexes of Pu(III) exist in solution, revisiting the Pu(III)/Cl system at the extremes of ionic strength may provide insight into the interaction between Pu(III) and Cl^- in solution.

Acknowledgment. This work was performed at Argonne National Laboratory operated by the University of Chicago, under the auspices of the United States Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under Contract W-31-109-ENG-38.

Supporting Information Available: Detailed crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060979A

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(25) Diffraction data were collected using a Bruker APEX II CCD equipped diffractometer. Structure solution and refinement were straighforward and carried out using *SHELXL-97*. Detailed crystallographic information is available in CIF format in the Supporting Information. Definitions of the *R* and *wR* factors are those defined by the International Union of Crystallography.

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