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Title: PLUTONIUM (IV) COMPLEXES OF MIXED PYRIDINE
N-OXIDE AND PHOSHINOXIDE F-ELEMENT
EXTRACTANTS

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Plutonium (IV) complexes of mixed pyridine N-oxide and phosphin oxide f-element extractants

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Introduction

Analytical and bulk scale separation and processing of aqueous acidic solutions containing f-element ions are regularly accomplished using liquid-liquid extraction (LLE) methods that employ a neutral organic donor ligand dissolved in an organic phase.¹⁻⁵ Several monofunctional ligands have been used as LLE reagents, but all display one or more deficiencies¹⁻⁵ due to the chemical similarity of the trivalent lanthanides (Ln) to the trivalent actinides (An). Since the trivalent 4f and 5f ions have identical charges, chemical separation agents for these two groups need to differentiate among these hard cations based on their size or chemical bonding preferences. This task is not easy since, as a consequence of the lanthanide and actinide contractions, the Ln and An fission products which need to be separated have similar ionic radii. In order to develop new ligands for the separation process, we must have a fundamental understanding of how these separation agents interact with both Ln and An ions on a molecular level. We have

prepared and are studying derivatives of the mixed pyridine N-oxide and phosphin oxide ligand family shown in Scheme 1. These compounds have been examined as LLE reagents in chloroform, arene, and alkane solvents, and they show favorable extraction performance for Ln(III) and Am(III) ions from strong HCl and HNO₃ solutions.^{6,7} The coordination ability of 2,6-bis[(diphenylphosphino)-methyl]benzene P,P'-dioxide (POPO) to Ln(III) ions has also been tested.⁸ Here 2:1 complexes are isolated, with POPO acting as a bidentate ligand. The extraction performance of POPO has not yet been characterized; however, it is expected to be a more weakly coordinating ligand compared to NOPO and NOPOPO given the absence of the N-oxide donor group.

Scheme 1: Organic oxide ligands for f-element extractions NOPO = 2-

(diphenylphosphino)pyridine N,P dioxide; POPO = 2,6-bis[(diphenylphosphino)-methyl]benzene P,P'-dioxide; NOPOPO = 2,6-bis(diphenylphosphinomethyl) pyridine-N,P,P'-trioxide).

Results and Discussion

In order to extend this work to tetravalent actinide ions, we are exploring the coordination chemistry of these oxygen donor ligands with Pu (IV). At this point, 2:1

complexes with *NOPOPO*,⁹ [(*NOPOPO*)₂Pu(NO₃)₂][NO₃]₂ (**1**), and *NOPO*,¹⁰ [Pu(*NOPO*)₂(NO₃)₃][Pu(NO₃)₆]_{0.5} (**2**), have been prepared and structurally characterized. In addition, initial Pu(IV) extraction data have been collected with derivatives of *NOPOPO*. These data indicate that Pu(IV) is more strongly extracted than Am(III) and Eu(III),¹¹ and suggest potentially useful LLE applications for the *NOPOPO* ligand. The coordination chemistry of the bifunctional ligand *POPO* with Pu(IV) has also been investigated. Two Pu(IV) compounds that contain the *POPO* ligand, Pu(*POPO*)(NO₃)₂Cl₂ (**3**) and Pu(*POPO*)(NO₃)₃(OMe) (**4**), have been prepared.

The organic oxide ligands shown in Scheme 1 were designed to preferentially coordinate actinide ions in order to efficiently separate An(III) and An(IV) from Ln(III) in acid using LLE methods. Strong tridentate coordination by the three oxide donors and the steric bulk of four phenyl groups characterize the *NOPOPO* ligand. The bidentate *NOPO* ligand also displays robust coordination but has much less steric bulk than *NOPOPO*, allowing the formation of 4:1 ligand to metal complexes in some Ln(III) systems.¹⁰ The steric demands of the *NOPOPO* ligand combined with the presence of an additional oxide functionality (which can occupy an additional coordination site on a metal) likely preclude the formation of analogous 4:1 ligand to metal *NOPOPO* coordination compounds. In contrast, the *POPO* ligand has approximately the same steric bulk as *NOPOPO*, but occupies one less coordination site due to replacement of the pyridine N-oxide functionality with a non-coordinating arene.

The *POPO* ligand can form 2:1 complexes with Ln(III) ions and structures for [(*POPO*)₂(Ln)(NO₃)₂]·0.5 MeOH (Ln = Er, Y) have been reported.⁸ In light of these results we attempted to prepare a 2:1 ligand to metal complex of *POPO* with Pu(IV). We

discovered that treatment of Pu (IV) in dilute nitric acid with two or more equivalents of *POPO* in methanol produced intractable products after solvent evaporation. However, slight modifications to these reaction conditions allowed us to isolate and characterize two distinct 1:1, *POPO*:Pu(IV) products.

Figure 1. Thermal ellipsoid plot of $(POPO)Pu(NO_3)_2Cl_2$ (**3**) at the 40% probability level. Selected bond distances (Å): Pu-O(1) 2.250(3), Pu-O(2) 2.238(3), Pu-O(4) 2.468(4), Pu-O(5) 2.452(4), Pu-O(7) 2.447(4), Pu-O(8) 2.465(4), Pu-Cl(1) 2.6000(3), Pu-Cl(2) 2.572(2).

The first product was obtained when the residue from a 2:1 reaction of *POPO* and Pu(IV) nitrate was dissolved in chloroform. Gradual evaporation of the chloroform produced orange crystals of $(POPO)Pu(NO_3)_2Cl_2$ (**3**). The chloride presumably comes from radiolytic or chemical degradation of chloroform. The structure of **3** was determined by X-ray crystallography and its ORTEP diagram is shown in Figure 1.

The second product was prepared by adding excess aqueous sodium hydroxide to a solution of excess *POPO* in methanol spiked with Pu (IV) nitrate stock. The sodium hydroxide was added in an attempt to sequester nitrate as NaNO_3 and encourage coordination of a second *POPO* ligand to the Pu(IV) center, but generates NaOMe instead. The methoxide ion effectively competes with nitrate for one coordination site on the Pu center and evaporation of the reaction solvent provides crystalline $(\text{POPO})\text{Pu}(\text{NO}_3)_3(\text{OMe})$ (**4**) as the only product. This result is not unexpected given the oxophilic nature of Pu(IV) and nucleophilicity of methoxide. However, it is surprising that coordination of two methoxide units is not observed especially when the synthesis of the dichloride complex **3** is taken into consideration. The structure of **4** was determined by X-ray crystallography and its ORTEP diagram is shown in Figure 2. This presentation will discuss the structural features of all the Pu(IV) complexes derived from the ligands in Scheme 1 and compare them to the Ln and An complexes that have been reported.

Figure 2. Thermal ellipsoid plot of $(POPO)Pu(NO_3)_3(OMe)$ (**4**) at the 40% probability level. Selected bond distances (Å): Pu-O(1) 2.301(2), Pu-O(2) 2.276(2), Pu-O(3) 2.497(3), Pu-O(4) 2.503(3), Pu-O(6) 2.530(3), Pu-O(7) 2.456(3), Pu-O(9) 2.487(3), Pu-O(10) 2.544(3), Pu-O(1M) 2.027(3).

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