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Coordination chemistry and extraction properties of phosphonopyridyl N,P oxides

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Abstract

The coordination chemistry of 6,6-bis(diphenylphosphinomethyl)-2,2′-bipyridine-*N,N′,P,P′*-tetra oxide with $Eu(NO_3)_3$ is described. The ligand forms a 2:1 complex in which both ligands bind in a tetradentate fashion to the metal. The liquid–liquid extraction of Am(III) in HNO_3 solutions by the ligand in $CHCl_3$ is also outlined. © 1998 Elsevier Science S.A.

Keywords: Ligands; Coordination complex; Americium extraction

1. Introduction

The coordination chemistry of phosphonopyridine *N,P*-oxides has recently been of interest in our group [1–3]. We have observed, for example, that ligand **1** and its derivatives bind in a bidentate fashion toward lanthanide ions despite the size of the resulting seven-membered chelate ring [1]. Furthermore, when provided in sufficient quantity (4:1 ligand/metal ratio) the neutral ligand displaces water and NO_3^- from the Ln(III) inner coordination sphere [1]. Ligand **2** and its derivatives are found to bind in a tridentate manner on Ln(III) ions producing 1:1 and 2:1 stoichiometry complexes [1]. In the latter cases, two nitrate ions are displaced to the outer coordination sphere. With the novel ligand **3**, tetradentate coordination has now been reported for several Ln(III) ions including La, Pr, Nd, Dy and Er, and all coordinated water and NO_3^- anions are displaced from the aquo ion by this powerfully chelating ligand [3]. A simplified view of the eight coordinate inner sphere (phenyl groups omitted for clarity) is shown in Fig. 1.

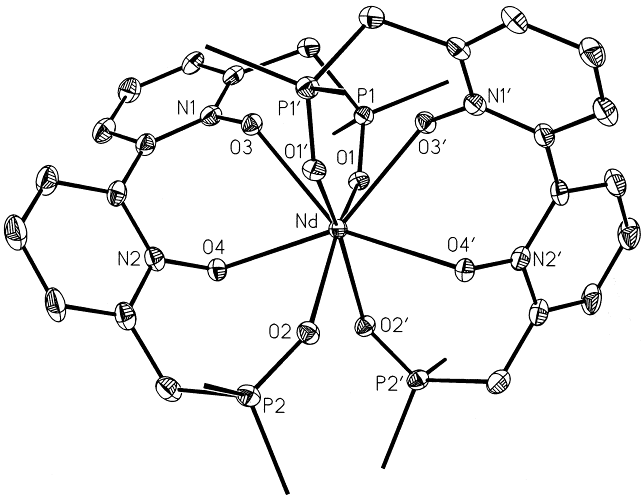
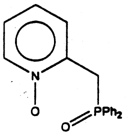


Fig. 1. View of the molecular structure of the inner coordination sphere of $[Nd(\mathbf{3})_2](NO_3)_3\cdot(DMF)_2$ (phenyl groups on the phosphorus atoms omitted for clarity).



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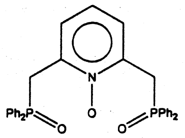

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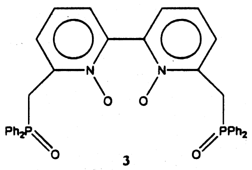

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Recently, we have begun to study the liquid–liquid extraction LLE behavior of these ligand types [4,5], and we report here the coordination behavior of **2** and **3** toward Eu(III), an Am(III) stand-in [6,7], and the subsequent initial findings of the LLE behavior of **3** with Am(III).

2. Experimental

2.1. Reagents

The ligands **2** and **3** (BNOPOPO) and the coordination complexes were prepared as described previously [1–3].

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The organic phase LLE solutions of **3** were prepared by dissolving weighed amounts of this ligand in chloroform. Chloroform was obtained from EM (Omnisolv) and was used without further purification. The nitric acid LLE solutions were prepared by using ultrapure water obtained from a Barnstead E pure-water purification system and ACS-grade nitric acid (J.T. Baker Chemical). The ^{241}Am(III), in dilute nitric acid, was obtained from Los Alamos National Laboratory stocks.

2.2. Nitric acid extractions

The chloroform solutions of **3** (1 or 2 ml, 0.125 M) were placed in 13×100-mm culture tubes. Acid solution (1 or 2 ml) was added to each and the phases were mixed with a vortex mixer for five min. The tubes were centrifuged and the aqueous fraction pipetted off and discarded. The organic phase was exposed twice more to the same procedure. Half of the retained organic phase was back-extracted three times with four times the volume of deionized water and the acid content of the combined water fractions was measured by titration with KOH. The ratio of the acid concentration to the ligand concentration $[HNO_3]_o/[BNOPOPO]_o$, both in the organic phase, is plotted against total acid concentration in Fig. 2.

2.3. Distribution ratios

The **3**/$CHCl_3$ organic phase was preequilibrated twice with an equal volume of the appropriate acid solution. Aliquots of the preequilibrated organic phase (1 ml) were placed into 13×100-mm Teflon screw cap culture tubes, and ^{241}Am/nitric acid solution (1 ml) was added to each tube. The two phases were mixed with a vortex mixer for one min, which was sufficient time to reach equilibrium. The two phases were centrifuged for five min and separated. Duplicate aliquots (typically 0.1 ml) of the organic and aqueous phases were placed into scintillation vials containing Packard Ultima-Gold XR scintillation fluid (14 ml) and deionized water (6 ml). The alpha activity of each phase was determined by counting each sample for 10 min by using a Packard 2500TR scintillation counter. The

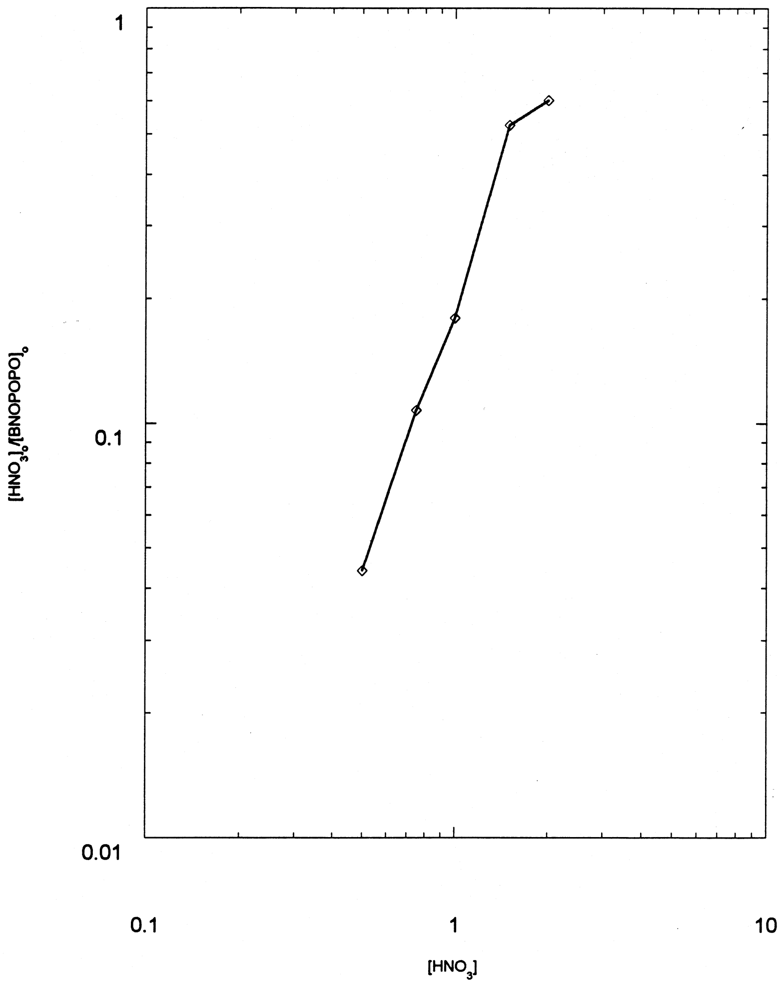

Fig. 2. HNO_3 extraction by **3** (0.125 M) in $CHCl_3$. Data are presented as a ratio of the acid concentration in the organic phase over the concentration of ligand $[HNO_3]_o/[BNOPOPO]_o$ vs. total nitric acid concentration $[HNO_3]$.

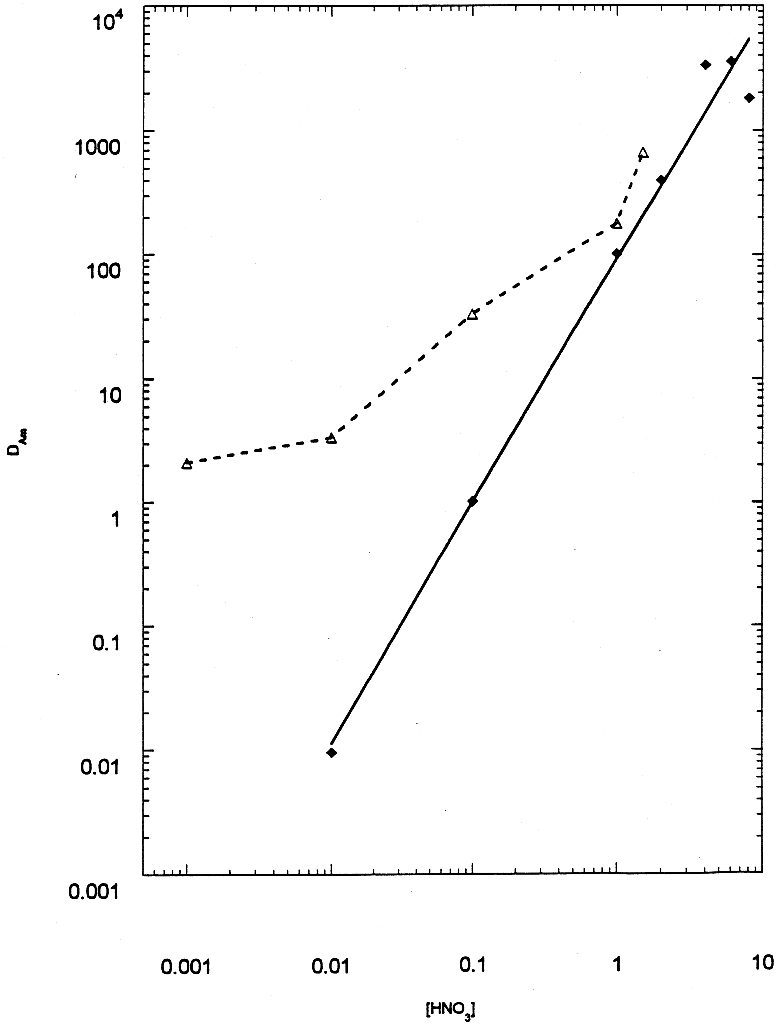

Fig. 3. Acid dependence of the extraction of Am(III) from HNO_3 solutions by **3** (0.125 M) in $CHCl_3$ (△, dashed line). Data for **3** are compared with results for **2** (0.05 M) in $CHCl_3$ (♦, solid line) reported previously [4].

Am(III) distribution ratios (D_{Am}s) were calculated by dividing the activity of the organic phase by the activity of the aqueous phase. The extractions were generally performed in triplicate, and individual data (△) presented in Fig. 3 represent average values from these measurements.

3. Results and discussion

Mixtures of **2** and $Eu(NO_3)_3(H_2O)_n$ in a 2:1 ratio of EtOH/$CHCl_3$ (2:1) form crystals of $[Eu(\mathbf{2})_2(NO_3)](NO_3)_2 \cdot (H_2O)_2(EtOH)_{0.5}$. The compound displays an IR spectrum with bands assigned to ν_{NO} and ν_{PO} at 1225 cm^{-1} and 1163 cm^{-1}, respectively. These values are in good agreement with data reported previously for a similar Yb complex [1]. The molecular structure of the complex is shown in Fig. 4. It is clearly apparent that **2** is acting as a tridentate chelating ligand with Eu(III). Indeed, the compound is isostructural with the $[Yb(\mathbf{2})(NO_3)](NO_3)_2]$ complex [1] and the metrical pa-

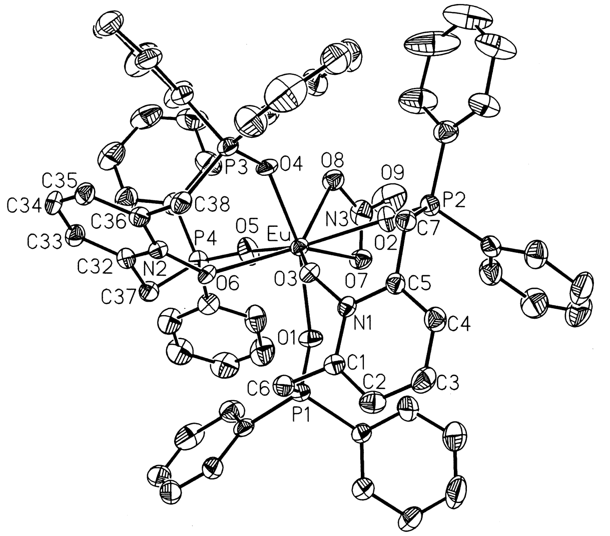

Fig. 4. View of the molecular structure of the inner coordination sphere of $[Eu(\mathbf{2})_2(NO_3)](NO_3)_2 \cdot (H_2O)_2 \cdot (EtOH)_{0.5}$ (phenyl-group labels omitted for clarity).

rameters are comparable between the two structures: Eu-O(N)$_{avg}$ 2.443(6) Å, Eu-O(P)$_{avg}$ 2.330(5) Å, N-O$_{avg}$ 1.335(7) Å and P=O$_{avg}$ 1.494(5) Å. The Eu-O(N) and Eu-O(P) distances are longer than the Yb-O(N) and Yb-O(P) distances, respectively, with differences larger than 3σ of the estimated standard deviations. This is to be expected since the smaller, more polarizing Yb(III) ion would be expected to pull the tridentate ligand **2** closer to it.

A combination of **3** with $Eu(NO_3)_3\cdot(H_2O)_n$ in a 2:1 ratio in DMF produces a crystalline solid of composition $[Eu(\mathbf{3})_2^{3+}](NO_3)_3\cdot(DMF)_2$ and elemental analyses (CHN) are in good agreement with this formula. IR spectra for the compound show a band at 1167 cm^{-1} assigned to the ν_{NO} stretch and a band at 1145 cm^{-1} assigned to the ν_{PO} stretch. Both are shifted from the respective values in the free ligand: 1209 cm^{-1} and 1190 cm^{-1}. These coordination shifts are comparable to those reported previously for the related Nd(III) complex [3]. Unfortunately, attempts to obtain single crystals of this complex were unsuccessful, but powder X-ray diffraction analysis indicates that the complex is isostructural with the Nd(III) structure pictured in Fig. 1. Hence we conclude that **3** is acting as a tetradentate ligand on Eu(III).

The extraction behavior of **3** relative to **2** is of great interest since **2** has proven to be a very effective extractant for trivalent Ln ions [4]. As found with **2**, it is important to study not only the metal ion binding with the ligand, but also the binding of HNO_3 since HNO_3 and Am(III) compete for the same coordination sites on the ligand. The results of HNO_3 extractions by **3** are summarized in Fig. 2. As shown, the ligand steadily extracts HNO_3 with increasing HNO_3 concentration (0.5 M–2 M). For simplicity, the amount of HNO_3 extracted is represented by the ratio $[HNO_3]_o/[BNOPOPO]_o$, which provides a mole ratio of acid to ligand. The increase is relatively linear from 0.5 M to 1 M HNO_3 and then begins to saturate. At the maximum the ligand extracts about 0.6 mole of HNO_3 per ligand. The changes in Am(III) distribution ratio as a function of HNO_3 concentration (dashed line, no activity correction used) toward a 0.125 M solution of **3** in $CHCl_3$ are shown in Fig. 3. Chloroform was used as the diluent since **3** does not show significant solubility in hydrocarbon solvents. The distribution ratios increase steadily from ~2 to 670 over the acid range, 1×10^{-3} M to 1.5 M HNO_3. Unfortunately, at 2.0 M HNO_3, the complex salts out forming a third phase. The steady increase of D_{Am} with increasing $[HNO_3]$ is similar to the behavior shown by ligand **2** [4]. Data for **2** at a lower ligand concentration (0.05 M) are included in Fig. 3. This is consistent with qualitative observations that both ligands form very stable complexes. Further studies of the ligand and NO_3^- dependencies on D_{Am} are in progress.

These preliminary findings indicate that ligands such as **3** may act as tetradentate chelates forming very stable complexes with Ln(III) ions. Further work is also in progress to develop hydrocarbon solvent soluble analogs and these ligands will be used to complete more detailed studies of extraction properties.

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