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Synthesis and Coordination Chemistry of 2-(Diethoxyphosphino)- and 2-(Diphenylphosphino)pyridine *N*,*P*-Dioxides. Crystal and Molecular Structures of Bis(nitrato)[2-(diethoxyphosphino)pyridine *N*,*P*-dioxide]dioxouranium(VI) and Bis(nitrato)[2-(diphenylphosphino)pyridine *N*,*P*-dioxide]dioxouranium(VI)

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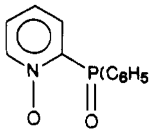
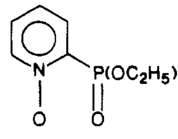
Bifunctional 2-(diphenylphosphino)pyridine *N*,*P*-dioxide, 2-[$(C_6H_5)_2P(O)]C_5H_4NO$ (**1**), and 2-(diethoxyphosphino)pyridine *N*,*P*-dioxide, 2-[$(C_2H_5O)_2P(O)]C_5H_4NO$ (**2**), were prepared by oxidation of the corresponding 2-(diphenylphosphino)pyridine *P*-oxide and 2-(diethoxyphosphino)pyridine *P*-oxide. The ligands were characterized by infrared and NMR spectroscopy, and the coordination chemistry toward $UO_2(NO_3)_2$ was examined. The complexes, $UO_2(NO_3)_2L$, were isolated and characterized, and the single-crystal X-ray diffraction analyses of $UO_2(NO_3)_2\{2\text{-}[(C_6H_5)_2P(O)]C_5H_4NO\}$ (**3**) and $UO_2(NO_3)_2\{2\text{-}[(C_2H_5O)_2P(O)]C_5H_4NO\}$ (**4**) were completed at 25 °C. Complex **3** crystallized in the triclinic space group $P\bar{1}$ with $a = 9.083$ (2) Å, $b = 10.644$ (1) Å, $c = 12.338$ (2) Å, $\alpha = 78.23$ (1)°, $\beta = 76.65$ (2)°, $\gamma = 76.74$ (1)°, $Z = 2$, $V = 1116.0$ Å^3, and $\rho_{calcd} = 2.05$ g/cm^3. The structure was solved by using heavy-atom techniques, and least-squares refinement converged at $R_F = 5.7\%$ and $R_{wF} = 7.8\%$ on 2514 independent reflections with $I > 2\sigma(I)$. The molecular structure of **3** was found to contain a linear UO_2^{2+} ion surrounded at its equator by four oxygen atoms from two bidentate nitrate ions and the phosphoryl and *N*-oxide oxygen atoms from one bidentate ligand. Several important bond distances include U–O(uranyl)$_{av}$ = 1.75 (1) Å, U–O(P) = 2.41 (1) Å, U–O(pyridine) = 2.38 (1) Å, P–O = 1.49 (1) Å, and N–O(pyridyl) = 1.33 (1) Å. Complex **4** crystallized in the triclinic space group $P\bar{1}$ with $a = 8.074$ (2) Å, $b = 10.514$ (2) Å, $c = 12.250$ (2) Å, $\alpha = 112.65$ (1)°, $\beta = 104.07$ (2)°, $\gamma = 92.11$ (2)°, $Z = 2$, $V = 921.0$ Å^3, and $\rho_{calcd} = 2.25$ g cm^{-3}. The structure was solved by heavy-atom techniques, and least-squares refinement converged at $R_F = 5.2\%$ and $R_{wF} = 6.3\%$ on 1989 independent reflections with $I \geq 2\sigma(I)$. The molecular structure of **4** was found to be closely related to the structure of **3** with the phosphonate pyridine *N*-oxide bonded in a bidentate fashion to the uranyl ion. Important bond distances include U–O(uranyl)$_{av}$ = 1.76 (1) Å, U–O(P) = 2.48 (1) Å, U–O(pyridine) = 2.35 (1) Å, P–O = 1.45 (1) Å, and N–O(pyridyl) = 1.37 (2) Å.

Introduction

Compounds containing monofunctional phosphoryl or carbonyl groups are known to be good extractants for lanthanide and actinide ions under selected conditions,[3] yet bifunctional (carbamoylmethyl)phosphonates and (carbamoylmethyl)phosphine oxides with P=O and C=O groups in 1,3-positions are found to be superior extractants, especially for Ln(III) and An(III) ions in strong-acid media.[4-6] It has also been shown that monofunctional pyridine *N*-oxide and substituted pyridine *N*-oxides can act as Ln and An ion extractants under various conditions.[7,8] On the basis of these observations and with our interest in designing new, selective extractants, it was appropriate to determine if bifunctional ligands with P=O and N—O groups in 1,3-combinations might also display favorable extraction properties. In this contribution, the syntheses of 2-(diphenylphosphino)pyridine *N*,*P*-dioxide (**1**) and 2-(diethoxyphosphino)pyridine *N*,*P*-dioxide (**2**) are described along with the coordination chemistry of each ligand with uranyl nitrate.



$Ph_2P(O)pyO$ (**1**)



$(EtO)_2P(O)pyO$ (**2**)

Experimental Section

General Information. Pyridine *N*-oxide, dimethyl sulfate, *n*-butyllithium, and diethyl phosphite were purchased from Aldrich Chemical Co., and diphenylphosphine and $UO_2(NO_3)_2\cdot 6H_2O$ were obtained from Strem Chemicals. All reactions, unless specified otherwise, were performed under dry nitrogen in Schlenk flasks or in glovebags. Infrared spectra were recorded on a Nicolet Model 6000 FTIR spectrometer, and NMR spectra were recorded on Varian FT-80A and GE-360 spectrometers. NMR standards were 85% H_3PO_4 (^{31}P) and Me_4Si (^1H, ^{13}C).

Preparations of Ligands. $(EtO)_2P(O)pyO$.[9] The synthesis employed was similar to the procedure described by Redmore.[10] Pyridine *N*-oxide (0.5 mol, 47.6 g) in a 250-mL Schlenk flask equipped with a magnetic stirbar was submerged in a water bath maintained at 20 °C. Under a constant nitrogen purge, dimethyl sulfate (0.5 mol, 63 g) was slowly added from a pressure-equalized dropping funnel to the vigorously stirred pyridine *N*-oxide. After addition was complete (1 h), the water bath temperature was raised and maintained at 60 °C for 2 h. The resulting dark brown, viscous oil was transferred to a dropping funnel. In a separate 250-mL Schlenk flask containing excess diethyl phosphite (120 g), sodium metal (0.5 mol, 11.5 g) was gradually added under a nitrogen purge. Once this reaction was complete (5 h), the flask was cooled to 0 °C and the brown oil was added over 3 h. The resulting mixture was

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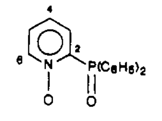
(9) Abbreviations used in the text include the following: py = pyridine; pyO = pyridine *N*-oxide; Ph = phenyl. The numbering scheme for the pyridyl ring assigns C_2 to the phosphonate-substituted carbon atom, and the remaining carbon atoms are sequentially numbered C_3–C_6:



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then allowed to warm slowly and was stirred overnight at 25 °C. Distilled water (150 mL) was added, the solution was extracted with $CHCl_3$ (3 × 150 mL), and the collected organic phases were back-extracted with 4 M HCl (2 × 100 mL). The collected aqueous phases were neutralized with concentrated NaOH solution, and the aqueous solution was extracted with $CHCl_3$ (2 × 150 mL). The collected chloroform solutions containing the product were evaporated in vacuo, and the remaining oil was subjected to vacuum distillation. 2-(Diethoxyphosphino)pyridine *P*-oxide, $(EtO)_2P(O)py$, distilled at 104–125 °C (25 mTorr); yield 26 g, 24%. A portion of 2-(diethoxyphosphino)pyridine *P*-oxide (0.025 mol, 5.4 g) in 12 mL of glacial acetic acid was cooled to 0 °C, and 30% hydrogen peroxide (6.0 mL) was added in one portion with stirring. After 15 min, the ice bath was removed and the solution warmed to 40 °C for 72 h. Distilled water (20 mL) was added and the resulting solution extracted with $CHCl_3$ (3 × 30 mL). The $CHCl_3$ extracts were vacuum-evaporated at 25 °C, leaving a yellow oil, yield 5.8 g, 100%. The product is greater than 95% pure. Further purification was accomplished by elution through a silica gel (60–200 mesh) column (2.5 cm × 60 cm) by using $CHCl_3$ or CH_2Cl_2 as the eluent.

$Ph_2P(O)pyO$. The precursor 2-(diphenylphosphino)pyridine was prepared exactly as described by Balch.[11] Oxidation was performed in two steps. Typically 2-(diphenylphosphino)pyridine (9.9 mmol, 2.6 g) in 10 mL of dry acetone was placed in a 200-mL Schlenk flask under nitrogen and cooled to 0 °C. Hydrogen peroxide (30%, 1.2 mL) was slowly added via syringe through a septum-capped side arm and the mixture stirred at 0 °C for 30 min. The majority of the acetone was vacuum-evaporated at 25 °C. To the resulting wet slurry was added 6 mL of glacial acetic acid, the mixture was cooled to 0 °C, and hydrogen peroxide (2.5 mL) was added. The mixture was stirred for 1 h at 25 °C and then overnight at 70 °C. The mixture was cooled and extracted with 50 mL of $CHCl_3$, the organic phase washed with distilled water, and the $CHCl_3$ phase collected and evaporated. The product is a pale yellow crystalline solid: yield 1.9 g, 65%; mp 144 °C.

Characterization of the Ligands. $(EtO)_2P(O)pyO$. Anal. Calcd for $PO_4NC_9H_{14}$: C, 46.70; H, 6.10; N, 6.06. Found: C, 45.14; H, 6.65; N, 5.67. Mass spectrum (*m/e*, (fragment) [relative intensity]): 232 ($M + H^+$) [7], 231 (M^+) [2], 186 ($PO_3NC_7H_9^+$) [8], 142 ($PO_2NC_5H_5^+$) [41], 105 (PO_3NC^+) [23], 79 ($NC_5H_5^+$) [100], 78 ($NC_5H_4^+$) [78]. Infrared spectrum (thin film, cm^{-1}): 2986 (m), 1718 (m), 1424 (m), 1284 (s), 1255 (s), 1144 (m), 1024 (s), 976 (m), 851 (m), 773 (m), 586 (m), 523 (m). NMR spectra (27 °C): $^{31}P\{^1H\}$ (neat) δ 4.6; $^{13}C\{^1H\}$ ($CDCl_3$)[9] δ 139.7 (J_{PC} = 216.9 Hz, C_2), 138.4 (J_{PC} = 6.0 Hz, C_6), 130.1 (J_{PC} = 10.3 Hz, C_4), 127.7 (J_{PC} = 2.0 Hz, C_3), 123.1 (J_{PC} = 10.9 Hz, C_5), 62.2 (J_{PC} = 6.1 Hz, OCH_2), 14.8 (J_{PC} = 6.1 Hz, CH_3).

$Ph_2P(O)pyO$. Anal. Calcd for $PO_2NC_{17}H_{14}$: C, 69.15; H, 4.78; N, 4.74. Found: C, 69.00; H, 5.43; N, 4.71. Mass spectrum (*m/e* (fragment) [relative intensity]): 295 (M^+) [8], 279 ($PONC_{17}H_{14}^+$) [71], 278 ($PONC_{17}H_{13}^+$) [82], 261 ($PNC_{17}H_{14}^+$) [3], 218 ($PO_2NC_{11}H_9^+$) [6], 203 ($POC_{12}H_{12}^+$) [10], 202 ($POC_{12}H_{11}^+$) [100], 201 ($POC_{12}H_{10}^+$) [26], 200 ($POC_{12}H_9^+$) [8], 199 ($POC_{12}H_8^+$) [18], 185 ($PC_{12}H_{10}^+$) [11], 78 ($NC_5H_4^+$) [51], 77 ($C_6H_5^+$) [65]. Infrared spectrum (KBr, cm^{-1}): 3057 (m), 1437 (s), 1421 (s), 1273 (s), 1186 (s). NMR spectra (27 °C): $^{31}P\{^1H\}$ ($CHCl_3$) δ 19.1; $^{13}C\{^1H\}$ ($CDCl_3$) δ 144.0 (J_{PC} = 115.2 Hz, C_2), 139.4 (C_6), 132.8 (J_{PC} = 9.3 Hz, C_4), 132.4 phenyl C), 132.1 (J_{PC} = 10.8 Hz, phenyl C), 129.6 (J_{PC} = 111.6 Hz, ipsophenyl C), 129.0 (C_3), 128.2 (J_{PC} = 13.6 Hz, phenyl C), 125.4 (J_{PC} = 7.9 Hz, C_5).

Preparation of the Complexes. $UO_2(NO_3)_2[(EtO)_2P(O)pyO]$. The complex was prepared by addition of 2 mmol of $UO_2(NO_3)_2 \cdot 6H_2O$ in 10 mL of ethanol to 2 mmol of $(EtO)_2P(O)pyO$ in 5 mL of diethyl ether. The solvents were slowly evaporated overnight, and the resulting solid was redissolved in CH_2Cl_2. Hexane was added to this solution until crystal growth was initiated. The complex is soluble in ethanol, $CHCl_3$, CH_2Cl_2, H_2O, and THF. Anal. Calcd for $UPO_{12}N_3C_9H_{14}$: C, 17.29; H, 2.26; N, 5.73; P, 4.95; U, 38.08. Found: C, 17.24; H, 2.39; N, 4.84; P, 5.11; U, 38.52. Infrared spectrum (KBr, cm^{-1}): 2986 (w), 1539 (s), 1521 (s), 1495 (m), 1288 (m), 1269 (m), 1227 (m), 1186 (m), 1154 (w), 1029 (s), 935 (s). NMR spectrum (27 °C, $CHCl_3$): $^{31}P\{^1H\}$ δ -0.3.

$UO_2(NO_3)_2[Ph_2P(O)pyO]$. The complex was prepared by addition of 2 mmol of $UO_2(NO_3)_2 \cdot 6H_2O$ in 10 mL of ethanol to 2 mmol of $Ph_2P(O)pyO$ in 10 mL of ethanol. The solution was mixed, and the ethanol and water were allowed to evaporate slowly. Suitable single crystals were obtained after 1 week. The crystals are soluble in ethanol, CH_2Cl_2, $CHCl_3$, and water. Anal. Calcd for $UPO_{10}N_3C_{17}H_{14}$: C, 29.62; H, 2.05. Found: C, 29.40; H, 2.29. Infrared spectrum (KBr, cm^{-1}): 3057 (m), 1493 (s), 1439 (m), 1427 (m), 1290 (s), 1279 (s), 1218 (m), 1144 (m), 1123 (m), 921 (s), 691 (m), 568 (m), 542 (m), 525 (m). NMR spectrum (27 °C, $CHCl_3$): $^{31}P\{^1H\}$ δ 31.1.

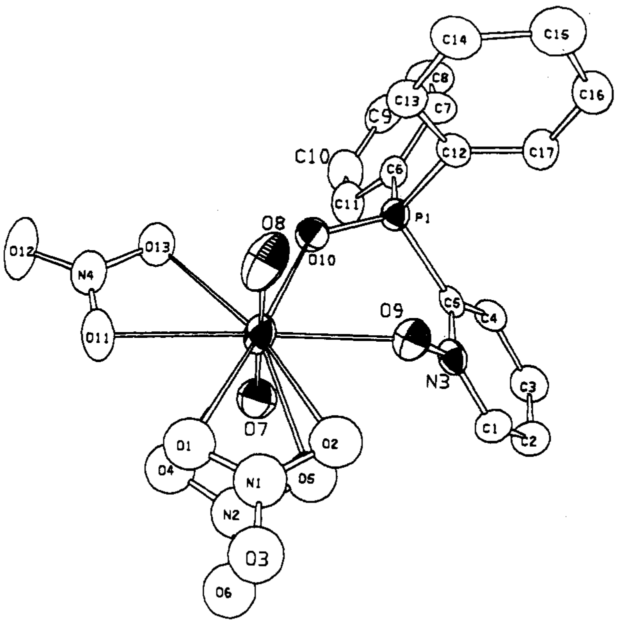

Figure 1. Molecular geometry and atom-labeling scheme for $UO_2(NO_3)_2\{2\text{-}[(C_6H_5)_2P(O)]C_5H_4NO\}$ (**3**, 50% ellipsoids). The disordered nitrate ion lies, on the average, symetrically half above and half below the least-squares equatorial plane of the uranyl ion.

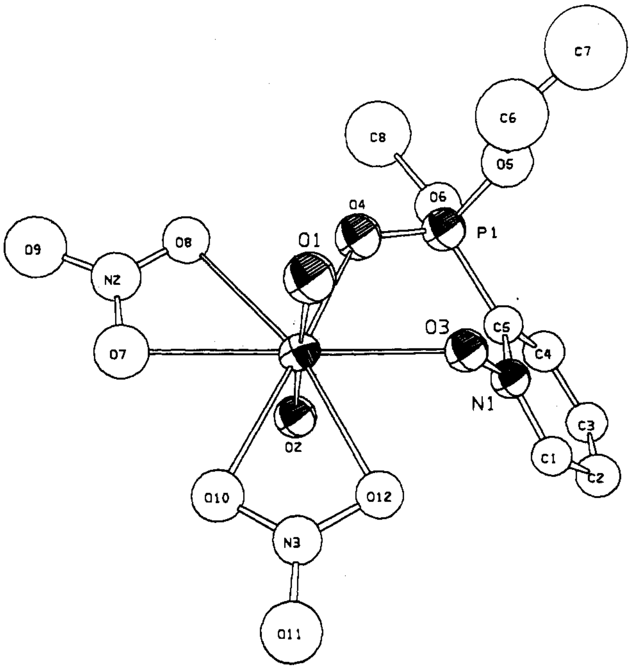

Figure 2. Molecular geometry and atom-labeling scheme for $UO_2(NO_3)_2\{2\text{-}[(C_2H_5O)_2P(O)]C_5H_4NO\}$ (**4**, 50% ellipsoids).

X-ray Diffraction Studies. Data were collected by variable-speed θ–2θ scans on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator and using Mo Kα radiation. Both structures were solved by using standard Patterson and difference Fourier methods and refined to the observed data ($I \geq 2\sigma(I)$) with full-matrix least-squares methods using appropriate neutral scattering factors and anomalous scattering terms.[12] Refinements included anisotropic thermal parameters for all atoms heavier than hydrogen and a correction for secondary extinction.[13] No attempt was made to locate hydrogen atoms in either

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(13) (a) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558–564. (b) Larson, A. C. *Ibid.* **1967**, *23*, 664–665. (c) Larson, A. C. In *Crystallographic Computing*; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, Denmark, 1970; pp 291–294.

Table I. X-ray Data

	3	**4**
chem formula	$C_{17}H_{14}N_3O_{10}PU$	$C_9H_{14}N_3O_{12}PU$
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.083 (2)	8.074 (2)
b, Å	10.644 (10)	10.514 (2)
c, Å	12.338 (2)	12.250 (2)
α, deg	78.23 (1)	112.65 (1)
β, deg	76.65 (2)	104.07 (2)
γ, deg	76.74 (1)	92.11 (2)
V, Å^3	1116.0	921.0
Z	2	2
D_{exptl}, g/Å^3	2.05	2.25
λ(Mo Kα_1), Å	0.709 30	0.709 30
temp, °C	25	25
cryst color	pale yellow	pale yellow
abs coeff, cm^{-1}	70.2	85.0
abs cor type	ϕ sphere	ϕ sphere
sphere radius, mm	0.2	0.2
transmission range	0.27, 0.07	0.12, 0.04
av peak width (ω), deg	0.7	0.7
scan range ($2\theta_{\max}$), deg	45	45
scan type	θ–2θ	θ–2θ
scan rate	variable	variable
$(-h,+h),(-k,+k),(-l,+l)$	(±9),(±11),(0,13)	(±8),(0,10),(±13)
total no. of reflecns collected	3076	2554
no. of unique reflecns	2913	2396
no. of reflecns with $I \geq 2\sigma(I)$	2514	1989
R_F equiv reflecns, %	3.6	2.7
R_F obsd reflecns, %	5.7	5.2
R_{wF} obsd reflecns, %	7.8	6.3
GOF	2.0	1.5

Table II. Fractional Coordinates for **3**

atom	x	y	z	B,[a] Å^2
U(1)	0.20476 (8)	0.18352 (5)	0.15062 (5)	6.09*
P(1)	0.1028 (4)	−0.1160 (4)	0.3025 (3)	4.8*
O(7)	0.393 (2)	0.101 (1)	0.107 (1)	9.2*
O(8)	0.016 (2)	0.264 (1)	0.193 (1)	9.0*
O(9)	0.104 (1)	0.029 (1)	0.088 (1)	6.1*
O(10)	0.167 (1)	0.002 (1)	0.300 (1)	5.8*
N(3)	0.172 (1)	−0.093 (1)	0.076 (1)	4.8*
C(1)	0.219 (2)	−0.122 (2)	−0.028 (1)	6.3*
C(2)	0.290 (2)	−0.250 (2)	−0.040 (1)	7.1*
C(3)	0.304 (2)	−0.348 (2)	0.054 (2)	7.7*
C(4)	0.244 (2)	−0.312 (1)	0.165 (1)	5.9*
C(5)	0.181 (1)	−0.184 (1)	0.173 (1)	4.3*
C(6)	0.157 (2)	−0.244 (1)	0.413 (1)	4.9*
C(7)	0.047 (2)	−0.313 (2)	0.487 (1)	6.2*
C(8)	0.088 (3)	−0.408 (2)	−0.575 (2)	8.8*
C(9)	0.243 (3)	−0.429 (2)	0.587 (2)	8.9*
C(10)	0.353 (2)	−0.362 (2)	0.516 (2)	9.1*
C(11)	0.311 (2)	−0.268 (2)	0.426 (2)	8.1*
C(12)	−0.105 (2)	−0.082 (1)	0.317 (1)	5.0*
C(13)	−0.184 (2)	0.030 (2)	0.361 (1)	6.2*
C(14)	−0.341 (2)	0.056 (2)	0.371 (2)	7.5*
C(15)	−0.422 (2)	−0.027 (2)	0.338 (2)	8.2*
C(16)	−0.331 (2)	−0.135 (2)	0.293 (1)	7.0*
C(17)	−0.174 (2)	−0.164 (2)	0.281 (1)	6.5*
N(1)	0.180 (2)	0.354 (1)	−0.066 (1)	7.7 (3)[b]
O(1)	0.236 (2)	0.378 (2)	0.010 (1)	7.7 (3)[b]
O(2)	0.123 (2)	0.253 (2)	−0.042 (1)	7.7 (3)[b]
O(3)	0.180 (2)	0.424 (2)	−0.155 (1)	7.7 (3)[b]
N(2)	0.298 (2)	0.326 (2)	−0.079 (2)	7.7 (3)[b]
O(4)	0.334 (4)	0.356 (3)	0.003 (2)	7.7 (3)[b]
O(5)	0.238 (4)	0.228 (2)	−0.058 (2)	7.7 (3)[b]
O(6)	0.321 (3)	0.389 (3)	−0.172 (2)	7.7 (3)[b]
N(4)	0.302 (2)	0.313 (2)	0.308 (1)	7.6*
O(11)	0.305 (2)	0.359 (1)	0.205 (1)	11.3*
O(12)	0.338 (2)	0.369 (1)	0.370 (1)	12.6*
O(13)	0.267 (1)	0.200 (1)	0.336 (1)	6.5*

[a] Values marked with an asterisk are given by $(U_{11} + U_{22} + U_{33})/3$. Anisotropic thermal parameters are published as supplementary data. [b] Disordered atoms.

Table III. Fractional Coordinates for **4**

atom	x	y	z	B,[a] Å^2
U(1)	0.26014 (8)	0.09414 (6)	0.21913 (6)	5.16*
P(1)	0.4174 (7)	0.4165 (5)	0.2162 (5)	7.5*
O(1)	0.456 (1)	0.071 (1)	0.304 (1)	7.0*
O(2)	0.067 (1)	0.119 (1)	0.130 (1)	6.5*
O(3)	0.421 (1)	0.132 (1)	0.096 (1)	7.0*
O(4)	0.352 (2)	0.346 (1)	0.283 (1)	8.5*
N(1)	0.360 (2)	0.185 (1)	0.010 (1)	6.4*
C(1)	0.316 (2)	0.095 (2)	−0.109 (2)	6.5*
C(2)	0.266 (2)	0.155 (2)	−0.199 (2)	8.1*
C(3)	0.248 (2)	0.293 (2)	−0.162 (2)	7.9*
C(4)	0.292 (3)	0.378 (2)	−0.036 (2)	8.9*
C(5)	0.351 (2)	0.323 (2)	0.053 (2)	6.5*
O(5)	0.613 (2)	0.449 (1)	0.251 (1)	10.1*
O(6)	0.354 (2)	0.558 (1)	0.234 (1)	10.0*
C(6)	0.737 (4)	0.384 (4)	0.316 (4)	21.5*
C(7)	0.894 (6)	0.420 (6)	0.327 (4)	23.5*
C(8)	0.341 (6)	0.706 (5)	0.371 (4)	17.6 (15)[b]
N(2)	0.137 (2)	0.163 (2)	0.440 (2)	8.0*
O(7)	0.108 (2)	0.044 (2)	0.355 (1)	10.0*
O(8)	0.219 (2)	0.250 (1)	0.421 (1)	7.9*
O(9)	0.095 (3)	0.188 (2)	0.532 (2)	14.2*
N(3)	0.178 (2)	−0.205 (2)	0.058 (1)	6.6*
O(10)	0.120 (2)	−0.150 (1)	0.149 (1)	8.8*
O(11)	0.138 (2)	−0.327 (1)	−0.007 (1)	9.9*
O(12)	0.278 (1)	−0.124 (1)	0.041 (1)	6.7*

[a] Values marked with an asterisk are given by $(U_{11} + U_{22} + U_{33})/3$. Anisotropic thermal parameters are published as supplementary data. [b] Disordered atom.

Table IV. Selected Interatomic Distances (Å) for $UO_2(NO_3)_2\{2\text{-}[(C_6H_5)_2P(O)]C_5H_4NO\}$ (**3**)

U–O(7)	1.75 (1)	N(3)–C(5)	1.38 (2)
U–O(8)	1.74 (1)	P(1)–C(6)	1.78 (1)
U–O(9)	2.38 (1)	P(1)–C(12)	1.82 (1)
U–O(10)	2.41 (1)	C(1)–C(2)	1.40 (2)
U–O(11)	2.52 (1)	C(2)–C(3)	1.41 (2)
U–O(13)	2.53 (1)	C(3)–C(4)	1.44 (2)
P(1)–O(10)	1.49 (1)	C(4)–C(5)	1.37 (2)
P(1)–C(5)	1.82 (1)	N(4)–O(11)	1.26 (2)
N(3)–O(9)	1.33 (1)	N(4)–O(12)	1.20 (2)
N(3)–C(1)	1.33 (2)	N(4)–O(13)	1.27 (2)

Table V. Selected Interatomic Distances (Å) for $UO_2(NO_3)_2\{2\text{-}[(C_2H_5O)_2P(O)]C_5H_4NO\}$

U–O(1)	1.75 (1)	N(1)–O(3)	1.37 (2)
U–O(2)	1.77 (1)	N(1)–C(1)	1.34 (2)
U–O(3)	2.35 (1)	C(1)–C(2)	1.45 (2)
U–O(4)	2.48 (1)	C(2)–C(3)	1.37 (3)
U–O(7)	2.49 (1)	C(3)–C(4)	1.40 (3)
U–O(8)	2.49 (1)	C(4)–C(5)	1.41 (2)
U–O(10)	2.49 (1)	O(5)–C(6)	1.48 (3)
U–O(12)	2.53 (1)	C(6)–C(7)	1.27 (6)
P(1)–O(4)	1.46 (1)	N(2)–O(7)	1.25 (2)
P(1)–O(5)	1.52 (2)	N(2)–O(8)	1.24 (2)
P(1)–O(6)	1.54 (1)	N(2)–O(9)	1.19 (2)
P(1)–C(5)	1.78 (2)	N(3)–O(10)	1.25 (2)
N(1)–C(5)	1.35 (2)	N(3)–O(11)	1.20 (2)
		N(3)–O(12)	1.26 (2)

structure. The Los Alamos crystal structure codes[14] were used for all calculations. Data were corrected for absorption by using the relative intensity of a low-angle reflection measured as a function of Ψ (corrected to ϕ) multiplied by a spherical correction using a radius calculated from the average distance between the three most prominent directions of crystal development. The function minimized was $R = \sum w^2[F_o - F_c]^2$, and weights were calculated as $w^2 = 4F^2/\sigma^2(I)$, where $\sigma(I) = \sigma_c(I) + (0.030I)^2$; $\sigma_c(I)$ is the error based on counting statistics. Lattice and data collection parameters are given in Table I. Coordinates and distances and angles are given in Tables II, IV, and VI for complex **3** and Tables III, V, and VII for complex **4**. ORTEP projections with appropriate numbering schemes are given in Figures 1 and 2.

$UO_2(NO_3)_2\{2\text{-}[(Ph)_2P(O)]pyO\}$ (3). Initial refinements clearly showed major peaks about one of the nitrate ions that indicated disorder. The

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Table VI. Selected Interatomic Bond Angles (deg) for $UO_2(NO_3)_2\{2\text{-}[(C_6H_5)_2P(O)]C_5H_4NO\}$

O(7)–U–O(8)	179.0 (5)	O(9)–N(3)–C(1)	118.5 (1.2)
O(7)–U–O(9)	90.4 (5)	C(1)–N(3)–C(5)	124.2 (1.3)
O(7)–U–O(10)	88.7 (5)	C(4)–C(5)–P(1)	126.1 (1.1)
O(7)–U–O(11)	91.0 (6)	C(5)–P(1)–C(6)	105.4 (6)
O(7)–U–O(13)	90.8 (5)	C(5)–P(1)–C(12)	106.5 (6)
O(8)–U–O(9)	88.6 (5)	C(6)–P(1)–C(12)	109.6 (7)
O(8)–U–O(10)	91.2 (5)	C(6)–P(1)–O(10)	111.3 (6)
O(8)–U–O(11)	90.0 (6)	N(3)–C(1)–C(2)	118.1 (1.5)
O(8)–U–O(13)	90.1 (5)	C(2)–C(3)–C(4)	117.8 (1.6)
O(9)–U–O(10)	70.0 (3)	C(1)–C(2)–C(3)	121.0 (1.5)
O(9)–U–O(11)	176.0 (4)		
O(9)–U–O(13)	134.1 (4)		
U–O(9)–N(3)	127.2 (8)	C(3)–C(4)–C(5)	118.9 (1.5)
U–O(10)–P(1)	129.8 (6)	C(4)–C(5)–N(3)	119.8 (1.3)
O(10)–P(1)–C(5)	110.6 (6)	O(11)–N(4)–O(13)	114.1 (1.4)
P(1)–C(5)–N(3)	114.1 (1.0)	O(11)–N(4)–O(12)	121.4 (1.7)
C(5)–N(3)–O(9)	117.2 (1.1)	O(12)–N(4)–O(13)	124.4 (1.8)

Table VII. Selected Interatomic Bond Angles (deg) for $UO_2(NO_3)_2\{2\text{-}[(C_2H_5O)_2P(O)]C_5H_4NO\}$

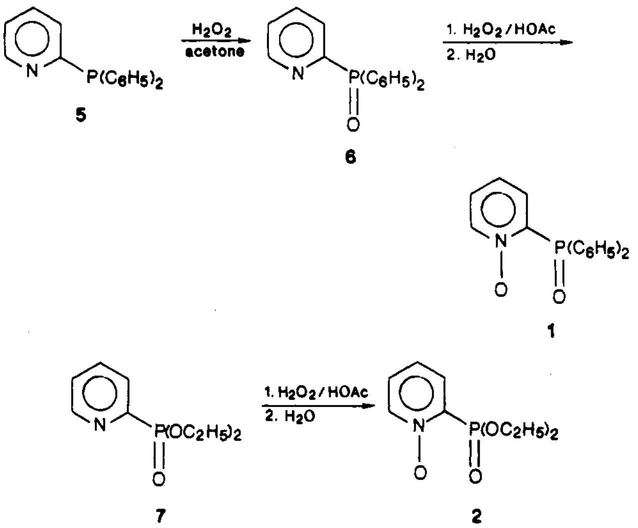
O(1)–U–O(2)	177.9 (6)	O(3)–N(1)–C(5)	116.6 (1.5)
O(1)–U–O(3)	85.5 (5)	O(3)–N(1)–C(1)	116.6 (1.3)
O(1)–U–O(4)	93.8 (5)	C(1)–N(1)–C(5)	126.8 (1.5)
O(1)–U–O(7)	90.2 (6)	N(1)–C(1)–C(2)	115.8 (1.6)
O(1)–U–O(8)	86.7 (5)	C(1)–C(2)–C(3)	120.7 (1.9)
O(1)–U–O(10)	94.6 (5)	C(2)–C(3)–C(4)	118.7 (1.8)
O(1)–U–O(12)	87.6 (5)	C(3)–C(4)–C(5)	121.4 (1.8)
O(2)–U–O(3)	92.4 (5)	C(4)–C(5)–N(1)	116.2 (1.8)
O(2)–U–O(4)	85.4 (5)	C(4)–C(5)–P(1)	127.3 (1.5)
O(2)–U–O(7)	91.9 (5)	C(5)–P(1)–O(5)	105.6 (0.9)
O(2)–U–O(8)	94.8 (5)	C(5)–P(1)–O(6)	102.7 (0.8)
O(2)–U–O(10)	86.4 (5)	O(5)–P(1)–O(6)	104.4 (0.9)
O(2)–U–O(12)	91.5 (4)	O(6)–P(1)–O(4)	114.2 (0.9)
O(3)–U–O(4)	68.3 (4)	O(5)–P(1)–O(4)	114.6 (0.9)
O(3)–U–O(7)	175.4 (4)	P(1)–O(5)–C(6)	125.7 (1.7)
O(3)–U–O(8)	131.9 (5)	O(5)–C(6)–C(7)	114.4 (3.6)
U–O(4)–P(1)	129.6 (8)	O(7)–N(2)–O(8)	113.4 (1.6)
U–O(4)–P(1)	129.6 (8)	O(7)–N(2)–O(9)	122.8 (1.9)
O(4)–P(1)–C(5)	114.2 (8)	O(8)–N(2)–O(9)	123.7 (1.8)
P(1)–C(5)–N(1)	117.1 (1.4)	O(10)–N(3)–O(12)	115.6 (1.4)
P(1)–C(5)–N(1)	117.1 (1.4)	O(11)–N(3)–O(12)	123.8 (1.7)

nature of the distances and angles among the difference peaks suggested that the disorder problem could be described by two nitrate ions. Final refinements were carried out by refining two appropriately placed nitrates as rigid bodies[15] with all thermal parameters on the two ions constrained to be equal and the population parameters on each constrained to be equal for all atoms. The sum of the overall population parameters was constrained to unity, and refinements converged to a population of 0.42 for nitrate 1 (N(1), O(1), O(2), and O(3)) and 0.58 for nitrate 2. Minor difference peaks remained in this region, but it was decided that more complicated models would not further resolve the problem. Previous experience with related disorder problems would indicate that attempts to resolve the present disorder problem by refining the structure in the space group $P\bar{1}$ would prove to be inconclusive. Therefore, these refinements were not attempted.

$UO_2(NO_3)_2\{2\text{-}[(EtO)_2P(O)]pyO\}$ (4). Final difference Fourier maps for this structure exhibited a rather large peak (2.9 e/Å^3) ca. 0.1 Å from the uranium atom and several smaller peaks ($\leq$1.0 e/Å^3) that either were very close to the uranium atom or were not in chemically interpretable positions. Note that the thermal parameter for C(8) is large and, although peaks appeared in the difference map which were at reasonable distances from C(8) for C–C bonds, the resulting C–C–O bond angles were very unreasonable. No further attempts were made to locate the terminal methyl carbon atom on C(8). Clearly, this omission has little effect on the most interesting aspect of the structure, i.e., that portion of the structure of the phosphoryl ligand which is involved with chelation of the uranyl ion.

Results and Discussion

Syntheses of 2-(diphenylphosphino)pyridine (**5**)[11] and 2-(diethoxyphosphino)pyridine *P*-oxide (**7**)[10] have been previously reported, and a limited amount of coordination chemistry of the phosphonate[16] and phosphine[11,17] has been accomplished. Prior to the present study, however, syntheses for the fully oxidized compounds 2-(diphenylphosphino)pyridine *N*,*P*-dioxide ($Ph_2P(O)pyO$, **1**) and 2-(diethoxyphosphino)pyridine *N*,*P*-dioxide ($(EtO)_2P(O)pyO$, **2**) had not been described. Both compounds were obtained in the present study in excellent yield by oxidation of the parent phosphine **5** or phosphonate **7** as outlined by the equations



Compounds **1** and **2** were obtained without byproduct formation (>95% purity),[18] and final purifications[5] were accomplished by column chromatography.

The compounds have been characterized by elemental analyses, mass spectrometry, and infrared and NMR spectroscopy. In particular, **1** and **2** display a strong N–O stretching vibration at 1273 and 1284 cm^{-1}, respectively, and these vibrations appear shifted to higher frequency compared to that of pyridine *N*-oxide,[19] 1250 cm^{-1}. The frequencies are also consistent with the phosphoryl groups in **1** and **2** acting as ortho electron-withdrawing groups on the parent pyridine *N*-oxide, which in turn would be expected to lower the effective pK_a value of the *N*-oxide group.[20,25] The phosphoryl, P=O, stretching frequency in **1** and **2** appears at 1186 and 1255 cm^{-1}, respectively. Similar down-frequency shifts for phosphoryl chromophores with increasing aryl replacement of alkoxy substituents have been observed for (carbamoylmethyl)phosphoryl ligands.[21-23] For example, ν_{PO} for the series $(EtO)_2P(O)CH_2C(O)NEt_2$, $(EtO)(Ph)P(O)CH_2C(O)NEt_2$, $Ph_2P(O)CH_2C(O)NEt_2$ and $(EtO)_2P(O)CH_2CO_2H$, (EtO)-

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(15) Rigid-body nitrate parameters were fixed at N–O(U) = 1.25 Å, N–O(terminal) = 1.20 Å, O(U)–N–O(U) = 116°, and O(U)–N–O(terminal) = 122°.

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(18) The intermediate phosphine oxide **6** can be isolated, and it has been partially characterized. Mass spectrum: 279 (M^+) [78]. NMR spectra (27 °C, $CHCl_3$): $^{31}P\{^1H\}$ δ 21.2; $^{13}C\{^1H\}$ δ 155.4 (J_{PC} = 132.3 Hz, C_2), 150.8 (J_{PC} = 20.8 Hz, C_6), 136.8 (J_{PC} = 8.8 Hz, C_4), 132.6 (J_{PC} = 103.4 Hz, ipso phenyl C), 132.6 (J_{PC} = 9.8 Hz, phenyl C), 132.5 (phenyl C), 128.9 (J_{PC} = 12.0 Hz, phenyl C), 128.7 (C_3), 125.9 (C_5).

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Table VIII. Comparative Structural Parameters for Uranyl Complexes

compd	U=O, Å	U–O(P), Å	P–O, Å	O–U–O, deg
$UO_2(NO_3)_2\{2\text{-}[(C_6H_5)_2P(O)]C_5H_4NO\}$ (**3**)	1.75 (1) 1.74 (1)	2.41 (1)	1.49 (1)	179.0 (5)
$UO_2(NO_3)_2\{2\text{-}[(C_2H_5O)_2P(O)]C_kH_4NO\}$ (**4**)	1.75 (1) 1.77 (1)	2.48 (1)	1.46 (2)	177.6 (6)
$UO_2(NO_3)_2[(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2]$ (**8**)	1.757 (5) 1.755 (6)	2.420 (4)	1.485 (5)	179.5 (2)
$UO_2(NO_3)_2[(EtO)(Ph)P(O)CH_2C(O)NEt_2]$ (**9**)	1.75 (1) 1.75 (1)	2.351 (7)	1.487 (9)	179.7 (5)
$UO_2(NO_3)_2[Ph_2P(O)CH_2C(O)NEt_2]$ (**10**)	1.742 (6) 1.742 (6)	2.377 (4)	1.512 (5)	178.6 (3)

$(Ph)P(O)CH_2CO_2H$, $Ph_2P(O)CH_2CO_2H$ decreases in the following orders: 1260, 1229, 1205 cm^{-1} and 1257, 1177, 1168 cm^{-1}. These trends are consistent with the phenyl groups attached to a phosphoryl group acting as better electron-releasing substituents, relative to alkoxy groups. Replacement of alkoxy groups with phenyl groups in turn should result in decreased effective P=O bond strength, increased phosphoryl oxygen atom base strength, and increased base strength of the *N*-oxide group.

The ^1H, ^{13}C, and ^{31}P NMR spectra have been assigned, and several observations are noteworthy. The $^{31}P\{^1H\}$ resonances for **1** and **2** appear as singlets at δ 19.1 and 4.6. These resonances appear shifted slightly upfield from the resonances in the respective phosphoryl pyridines, **6** and **7**, δ 21.2 and 9.9. The high-field position of **2** relative to the position of **1** is a trend typically found in comparisons of phosphorus chemical shifts for phosphonates and phosphine oxides.[21-24] The $^{13}C\{^1H\}$ NMR spectra show distinct resonances for each carbon in the pyridyl ring. Carbon 2 in **1** and **2** appears at δ 144.0 (J_{PC} = 115.2 Hz) and 139.7 (J_{PC} = 216.9 Hz). The large coupling constants are consistent with the bonding of the phosphorus to an sp^2-hybridized carbon atom. The decrease in J_{PC} with increasing phenyl substitution has also been seen in (carbamoylmethyl)phosphoryl compounds.[21,22] The ^{13}C shifts and coupling constants also can be compared with data from the precursors **6**, δ 155.4 (J_{PC} = 132.3 Hz, C_2)[18] and **7**, δ 151.0 (J_{PC} = 225 Hz, C_2).

Combinations of $UO_2(NO_3)_2{\cdot}6H_2O$ with **1** and **2** in ethanol/ether or ethanol solutions result in the formation of the yellow crystalline solids $UO_2(NO_3)_2(Ph_2P(O)pyO)$ (**3**) and $UO_2(NO_3)_2((EtO)_2P(O)pyO)$ (**4**). Elemental analyses confirm the 1:1 ligand:metal stoichiometry for the complexes. Infrared spectra, obtained from KBr pellets, show a medium-intensity ν_{NO} band at 1218 and 1227 cm^{-1}, respectively. These are shifted down-frequency from the signals for the free ligands: **3**, $\Delta\nu_{NO} = -55$ cm^{-1}; **4**, $\Delta\nu_{NO} = -57$ cm^{-1}. Metal ion complexation of pyridine *N*-oxides has been previously observed to induce down-frequency ν_{NO} shifts of 10–80 cm^{-1} relative to the uncoordinated ligand, and this effect has been exhaustively studied.[25] Specifically, in several series of UO_2Cl_2L and $UO_2(ClO_4)_2L$ complexes (L = para-substituted pyridine *N*-oxides), the ranges of $\Delta\nu_{NO}$ values are −5 to −34 and −2 to −51 cm^{-1} [20,26] and the shifts are dependent upon the electronic character of the para substituent group. The large shifts for **3** and **4** clearly indicate a relatively strong interaction between the *N*-oxide site and uranyl ion. The infrared spectra also show medium-intensity ν_{PO} bands: **3**, 1144 cm^{-1}; **4**, 1186 cm^{-1}. The coordination shifts, $\Delta\nu_{PO}$, of 42 and 69 cm^{-1} can be compared with $\Delta\nu_{PO}$ values for the uranyl complexes $UO_2(NO_3)_2L$, L = $(EtO)_2P(O)CH_2C(O)NEt_2$, $(EtO)(Ph)P(O)CH_2C(O)NEt_2$, and $Ph_2P(O)CH_2C(O)NEt_2$, 61, 56, and 60 cm^{-1}, respectively. The shifts for **3** and **4** also are consistent with strong phosphoryl coordination to the uranyl ion.

The asymmetric uranyl stretching frequency in **3** and **4** appears at 921 and 935 cm^{-1}, respectively. These frequencies can be compared with ν_{OUO} in the series of $UO_2(NO_3)_2L$ (L = (carbamoylmethyl)phosphoryls) complexes listed above: 943, 930, and 925 cm^{-1}. Carnall[27] and Peppard[28] have suggested that the magnitude of the uranyl asymmetric stretch can be related to the electron density provided by coordinated ligands on the UO_2^{2+} group. Furthermore, it appears that as the uranyl–ligand bond strength increases, the ν_{OUO} frequency decreases. The noticeably lower ν_{OUO} frequency in **3** is consistent with **1** acting overall as a slightly more strongly coordinating ligand.

Crystal structure determinations for **3** and **4** confirm the stoichiometry of the complexes as $UO_2(NO_3)_2L$. In addition, they indicate that the phosphoryl pyridine *N*-oxides act as bidentate ligands. The structures of **3** and **4** are closely related, and they are similar in some respects to the structures of $UO_2(NO_3)_2[(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2]$ (**8**),[29] $UO_2(NO_3)_2[(EtO)(Ph)P(O)CH_2C(O)NEt_2]$ (**9**),[21] and $UO_2(NO_3)_2[Ph_2P(O)CH_2C(O)NEt_2]$ (**10**).[21] Selected structural parameters for these complexes are summarized in Table VIII. In **3** and **4**, the uranyl groups are linear, and they are surrounded by a six-atom oxygen belt provided by two bidentate nitrate groups and a bidentate phosphoryl pyridine *N*-oxide ligand. The eight oxygen atoms form an irregular hexagonal bipyramid, which resembles the coordination polyhedra in **8**–**10** as well as in several other uranyl complexes.[21,29] The uranyl U=O distances in **3** and **4** are the same within experimental error and essentially equivalent to U=O distances in **8**–**10** as well as in $UO_2(NO_3)_2[(C_4H_9)_3PO]_2$[30] (1.742 (7) Å) and $UO_2(NO_3)_2(H_2O)_2$[31] (1.763 (5) and 1.754 (4) Å). As found with **8**–**10**, the accuracy of the uranyl U=O bond distance determinations are not high enough for **3** and **4** to test whether there is a correlation of these distances with the donor strength of the ligand L.

The U–O(phosphoryl) bond distances for **3** (2.41 (1) Å) and **4** (2.48 (1) Å) are comparable with U–O(phosphoryl) distances in **8**–**10** and in $UO_2(NO_3)_2[(C_4H_9)_3PO]_2$ (2.347 (6) Å) and $UO_2(OAc)_2[Ph_3P(O)]_2$[32] (2.37 (3) Å). If bond distances in closely related complexes, e.g., **8**–**10**, can be utilized to provide an approximate order in coordinate bond strength, hence phosphoryl oxygen atom donor strength, then it would appear that the uranyl–phosphoryl oxygen atom interactions in **3** and **4** are at the longer, weaker end of this series of complexes. It is worth noting also that the slightly shorter U–O(phosphoryl) distance in **3** is consistent with the expected greater basicity for this oxygen due to the arryl groups on phosphorus. The P=O distances in **3** (1.49 (1) Å) and **4** (1.45 (1) Å) also are similar with the distances in **8**–**10** and in $UO_2(NO_3)_2[(C_4H_9)_3PO]_2$ (1.489 (7) Å).

The U–O(*N*-oxide) and N–O bond distances in **3** (U–O(9) = 2.38 (1) Å, N(3)–O(9) = 1.33 (1) Å) and **4** (U–O(3) = 2.35 (1) Å, N(1)–O(3) = 1.37 (2) Å) are comparable with distances found in several uranyl complexes containing pyridine *N*-oxide ligands. Several examples include (2,6-dicarboxylatopyridine *N*-oxide)dioxouranium(VI) trihydrate[33] (U–O = 2.32 (1) Å and N–O = 1.34 (2) Å), (dimethyl sulfoxide)bis(1-oxo-2-thiopyridinato)di-

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oxouranium(VI)[34] (U–O = 2.34 (1), 2.31 (1) Å and N–O = 1.35 (2), 1.36 (2) Å), and aquabis(1,2-dioxopyridinato)dioxouranium hydrate[34] (U–O = 2.35 (1) Å and N–O = 1.38 (2) Å). Notice also that the U–O(*N*-oxide) distances in **3** and **4** are significantly shorter than the U–O(P) distances. This is qualitatively consistent with the *N*-oxide acting as the stronger base site.

The chelate rings in **8–10** are approximately shaped in a chair cyclohexane ring conformation with the U—O═C bond angle greater than the U—O═P bond angle: **8**, 137.6 (5) and 132.6 (3)°; **9**, 140.7 (7) and 136.2 (6)°; **10**, 141.0 (5) and 135.3 (3)°. The ligand "bite" angles (C)O–U–O(P) and nonbonded "bite" distances are 70.4 (2), 70.6 (3), and 71.8 (2)° and 2.781, 2.760, and 2.803 Å, respectively. In **3** and **4**, on the other hand, the chelate rings have a more irregular "twist-chair" cyclohexane configuration with the U—O═P bond angle slightly larger than the U–O–N bond angle: **3**, 129.8 (6) and 127.2 (8)°; **4**, 129.6 (9) and 124.0 (8)°. The bite angles (N)O–U–O(P) and nonbonded bite distances N(O)···(O)P are 70.0 (3)° and 2.742 Å for **3** and 68.3 (4)° and 2.716 Å for **4**. The bite size represents ca. the O···O van der Waals distance in these ligands, a feature that may dictate the dihederal angle between the pyridyl ring and the plane defined by e.g. O(10), P, and C(5) in **3** of approximately 52°. Clearly rotation about the P–C(pyridyl) bond to achieve planarity of the O–P–C–N–O moiety would bring these two oxygen atoms much closer together. In addition, in both structures both the phosphorus and nitrogen atoms of the ligand lie to the same side of the equatorial plane of the uranyl moiety, (0.9 and 0.2 Å, respectively). Obvious differences in packing in the two structures would weaken arguments for this feature based on molecular packing. These structural features in the chelate rings and mode of attachment to the uranyl ion clearly distinguish the (carbamoylmethyl)phosphoryls from the phosphoryl pyridine *N*-oxides in their respective uranyl complexes, and it is of interest to determine if similar differences appear in the structures of lanthanide complexes. It remains to be determined if this structural feature will correlate with differences in extraction abilities for the respective families of ligands.

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Supplementary Material Available: Tables SI and SII listing thermal parameters, Table SIII listing phenyl ring distances and angles, and Figures SI and SII showing chelate ring core structures (7 pages); Tables SIV and SV listing calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

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Interlayer Coordination Environments of Iron, Cobalt, and Nickel in Vanadyl Phosphate Dihydrate, $VOPO_4\cdot 2H_2O$, Intercalation Compounds

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The results of both structural and spectroscopic studies carried out upon vanadyl phosphate dihydrate ($VOPO_4\cdot 2H_2O$) intercalation compounds containing iron, cobalt, and nickel are reported. The approximate stoichiometries of these layered compounds are $Fe_{2/5}VOPO_4\cdot 3H_2O$ (**1**), $Co_{1/5}VOPO_4\cdot 2H_2O$ (**2**), and $Ni_{1/5}VOPO_4\cdot 2H_2O$ (**3**). By the use of EXAFS (extended X-ray absorption fine structure), the structures in the immediate vicinity of the transition-metal ion intercalants (Fe, Co, Ni) in **1–3** were determined. The EXAFS results indicate that Fe^{3+} ions in **1** and Co^{2+} ions in **2** have four oxygen nearest neighbors at 1.95 (2) and 2.03 (1) Å, respectively, whereas Ni^{2+} ions in **3** have six oxygen nearest neighbors at 2.05 (2) Å. In addition, there is a second, distant shell of approximately eight oxygen atoms around the Ni^{2+} ions in **3** at 3.02 (4) Å. Powder X-ray diffraction (XRD) measurements show that the V–P–O interlayer distance contracts upon intercalation; that for the pristine $VOPO_4\cdot 2H_2O$ parent compound is 7.40 (2) Å, whereas those for **1–3** are 6.64, 6.67, and 6.84 (±0.02) Å. A comparison of the infrared (IR), Raman, and XRD data for **1–3** and the parent compound reveals a decrease in short-range order as well as crystallinity upon intercalation. The iron intercalate (**1**) exhibits the greatest structural modification and lattice disorder. In the IR and Raman spectra for **1–3** and $VOPO_4\cdot 2H_2O$, $[V—O]^{2+,3+}$, $[V{=}O]^{2+,3+}$, and P—O vibrations all occur between ca. 800 and 1250 cm^{-1}. Raman band frequency shifts that occur upon intercalation by iron, cobalt, and nickel are correlated with the reduction of vanadium in the parent lattice. The thermal analyses of these intercalates, as well as an examination of the infrared OH stretching (3300–3600 cm^{-1}) and bending (1620 cm^{-1}) modes, show differences in the hydration among **1–3**. On the basis of the available structural (EXAFS, XRD) and spectroscopic (IR, Raman) data for **1–3**, we address the interlayer site occupancies of the transition-metal ion intercalants with reference to the structure of the parent V–P–O lattice.

Introduction

Compounds with layered structures have attracted considerable attention,[1] especially for their potential practical applications as solid ionic conductors (electrolytes), anisotropic electronic conductors, inorganic ion exchangers, cathode materials, and catalysts. In particular, experimental and theoretical activity has focused upon the physical properties of intercalation compounds of lamellar inorganic solids.[2–4] The most extensively studied intercalation compounds of quasi-two-dimensional, layered materials include those obtained from iron oxychloride[5–8] (FeOCl), transition-metal

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