

qualitative considerations. Inclusion of sulfur d orbitals increases the calculated electron affinities by approximately 0.8 eV in both systems. In contrast to the ESR results, addition of an electron to a ligand orbital is favored by 0.2–0.4 eV over the addition of the electron to the Ni d_{xy} orbital in Ni(Et₂dtc)₂.²⁰ Since the geometry of the anion may be sensitive to the nature of the MO containing the odd electron, differential relaxation of geometry in the two anion states could cause the energies to change by the small amount necessary to alter the ground state of the anion.²¹ On the basis of the calculated electron affinities, Ni(pdctc)₂⁻ is less likely to contain the odd electron in a metal-based orbital than is Ni(Et₂dtc)₂⁻.

Our ΔE (SCF) calculations confirm that Ni(Et₂dtc)₂ is more readily oxidized than Ni(pdctc)₂ (Table VI). The lowest energy one-hole state results from removal of the electron from a lower energy d_{z^2} orbital, not the highest occupied MO. This indicates that the complex Ni(Et₂dtc)₂⁺ produced initially upon oxidation contains nickel(III). Ni(R₂dtc)₂ complexes are known to undergo irreversible oxidation to Ni(R₂dtc)₃⁺ by means of nickel(III) intermediates.^{17,22} It is not clear, however, whether direct oxidation to Ni(R₂dtc)₂⁺ is important in the mechanism.

Our calculations suggest that neither complex will be susceptible to electrophilic decomposition. The two highest occupied MO's in Ni(pdctc)₂ are composed primarily of p_z orbitals on the carbon atoms of the pyrrole rings. Electrophilic attack involving these MO's does not directly affect the Ni–S fragment of the molecule. Furthermore, the HOMO's of Ni(Et₂dtc)₂ contain appreciable Ni–S antibonding character. Therefore, attack by an electrophile should *strengthen*, not weaken, the Ni–S bond in this system.

The LUMO's of Ni(Et₂dtc)₂ are composed primarily of C–N p_z antibonding character, whereas the N p_z orbital contributes much less to the LUMO of Ni(pdctc)₂. The C–S antibonding characters of the LUMO's are similar in the two complexes. Attack of a nucleophile should weaken the C–N bond of Ni(Et₂dtc)₂ but not affect the C–N bond of Ni(pdctc)₂.

Acknowledgment. We thank Prof. Michael C. Zerner for providing us with a copy of his INDO program and Wendy Lou Elcesser for helpful suggestions during the preparation of the manuscript.

Appendix

Parameters were taken from ref 12 and 13 with the following exceptions: $\beta_{3d}(\text{Ni}) = -28.0$ eV; $\beta_{3d}(\text{S}) = -4.0$ eV; $f_r = 0.610$. The coordinates for Ni(Et₂dtc)₂ were taken from the published crystal structure²³ and idealized to C_{2h} symmetry. Bond lengths used were Ni–S = 2.20 Å, C–S = 1.706 Å, and C–N = 1.326 Å. The coordinates of the pdtc group in Ni(pdctc)₂ were based on the crystal structure of Fe(pdctc)₃.⁴ The geometry of the complex was idealized to D_{2h} symmetry. Bond lengths used were Ni–S = 2.20 Å, C–S = 1.681 Å, and C–N = 1.378 Å. The same bond lengths were used in the free-ligand calculations as in the metal complexes. No geometry optimizations were performed. All calculations on the closed-shell systems were of the restricted Hartree–Fock (RHF) type. Unrestricted Hartree–Fock (UHF) calculations were performed on the open-shell systems. The odd electron was assigned to various molecular orbitals to obtain energies of different one-hole states. Reported energies involving UHF calculations do not include spin annihilation. Ionization energies and electron affinities are obtained from ΔE (SCF) calculations by taking the difference in total energy between the molecular ion and the neutral molecule.

(20) There is some spin contamination in both UHF states of Ni(Et₂dtc)₂⁻. The values of S^2 are 0.76 and 0.80 for the ²B_g and ²B_u states when no sulfur d orbitals are included and 0.78 and 0.80 when sulfur d orbitals are present in the calculation. However, the energy of the ²B_g state is still 0.3 eV higher than that of the ²B_u state even after spin annihilation.

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Synthesis and Coordination Chemistry of 2-(Diisopropoxyphosphino)pyridine *N,P*-Dioxide. Crystal and Molecular Structure of Bis[2-(diisopropoxyphosphino)pyridine *N,P*-dioxide]lanthanum Nitrate

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Ligands with donor oxygen atoms in 1,3-positions are normally found to be good chelating groups for hard transition metal ions, and classical examples are found in the family of acetylacetonate ligands. For the trivalent lanthanide and actinide ions, methylenediphosphonates and (carbamoymethyl)phosphonates with two P=O or P=O and C=O groups in 1,3-positions have been found to form many coordination complexes, as well as display useful extraction applications.^{2–6} Extending this concept, there has been interest in developing new families of ligands containing a P=O group and a functionality, X–O where X is N or S, since these combinations might be expected to show selective coordination properties. Following this reasoning, we recently reported on the synthesis of 2-(diethoxyphosphino)pyridine *N,P*-dioxide and 2-(diphenylphosphino)pyridine *N,P*-dioxide.⁷ These ligands were found to form complexes with the uranyl ion, UO₂(NO₃)₂·L, in which L was bonded to uranium in a bidentate coordination mode. We report here on the preparation of 2-(diisopropoxyphosphino)pyridine *N,P*-dioxide and its coordination chemistry with the early lanthanide La(NO₃)₃.

Experimental Section

General Information. Pyridine *N*-oxide, dimethyl sulfate, *n*-butyllithium, and triisopropyl phosphite were purchased from Aldrich Chemical Co., and La(NO₃)₃·6H₂O was obtained from Alfa Products (Ventron). 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 measured on a Varian FT-80A spectrometer. NMR standards were 85% H₃PO₄ (³¹P) and Me₄Si (¹H, ¹³C).

Ligand Preparation. The synthesis employed was similar to that described previously for the ethoxy and phenyl analogues.⁷ However, there are several important differences, and the procedure is outlined here. Pyridine *N*-oxide (26.0 g, 0.273 mol) in a 250-mL Schlenk flask equipped with a stir bar was submerged in a water bath maintained at 20 °C. Under a nitrogen purge, dimethyl sulfate (25.9 mL, 0.273 mol) was slowly added to the vigorously stirred pyridine *N*-oxide. After addition was complete (1 h), the water bath temperature was increased to 60 °C and held for 2 h. The resulting brown oil was transferred to a dropping

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Table I. X-ray Data for $\text{La}(\text{NO}_3)_3 \cdot 2\text{-}[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{C}_5\text{H}_4\text{NO}]_2$

chem formula	$\text{C}_{22}\text{H}_{36}\text{N}_5\text{O}_{17}\text{P}_2\text{La}$
cryst system	monoclinic
space group	$C2/c$
a , Å	17.440 (9)
b , Å	9.325 (2)
c , Å	23.267 (8)
β , deg	110.64 (4)
V , Å ³	3540.9
Z	4
C_x , g/cm ³	1.582
$\lambda(\text{Mo K}\alpha_1)$	0.70930
temp, °C	23
cryst color	white (colorless)
cryst dimens, mm	$0.2 \times 0.2 \times 0.3$
abs coeff, cm ⁻¹	13.71
abs cor type	ϕ sphere
transmission: min, max	0.73, 0.36
av peak width (ω), deg	1.0
scan range (2θ max), deg	45
scan type	$\theta-2\theta$
scan rate	variable
$(-h,+h),(-k,+k),(-l,+l)$	(0,18),(0,10),(24,23)
total no of reflns	2403
no. of unique reflns	2316
no of reflns with $I \geq 2\sigma(I)$	1982
$R_F(\text{equiv reflns})$, %	2.2
$R_F(\text{obsd reflns})$, %	5.0
$R_w F(\text{obsd reflns})$, %	6.2

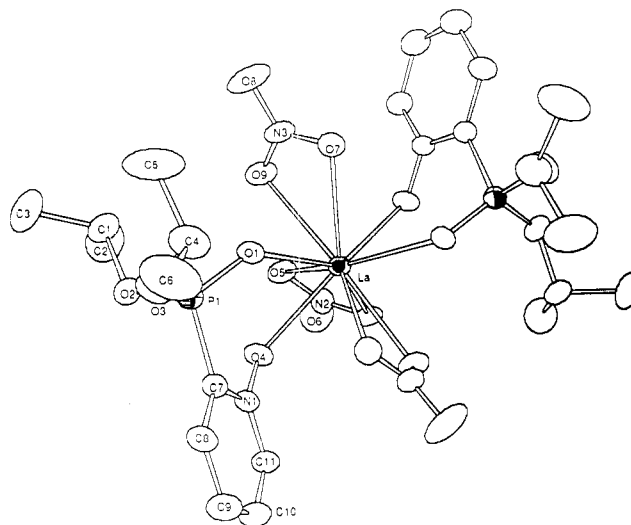
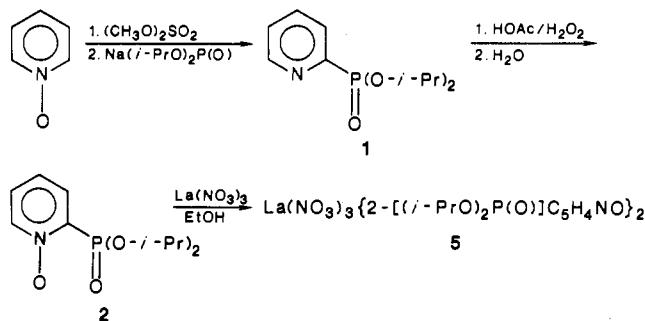
funnel. In a separate flask, triisopropyl phosphite (45.6 mL, 0.273 mol) was slowly dripped into a THF (50 mL) slurry of NaH (6.9 g, 0.29 mol) held at 0 °C. The mixture was stirred overnight and then filtered to remove excess NaH. The brown oil was slowly combined (3 h) with the filtrate, and the mixture was stirred overnight.⁷ The oily product was distilled twice through a 6-in. Vigreux column. The product was 2-(diisopropoxyphosphino)pyridine *P*-oxide (**1**): bp 90–91 °C (14 mTorr); yield 7.9 g, 12%. This material was oxidized with glacial acetic acid and hydrogen peroxide exactly as described earlier,⁷ and the final product, 2-(diisopropoxyphosphino)pyridine *N,P*-dioxide (**2**), was obtained in quantitative yield as a light yellow oil.

Characterization of the Ligands. $[(i\text{-PrO})_2\text{P}(\text{O})\text{C}_5\text{H}_4\text{N}]$ (**1**). Anal. Calcd for $\text{PO}_3\text{NC}_5\text{H}_8$: C, 54.32; H, 7.46; N, 5.76. Found: C, 54.03; H, 7.68; N, 5.63. Mass spectrum [m/e (fragment) [relative intensity]]: 244 ($M + 1^+$) [2], 185 ($\text{PO}_2\text{NC}_5\text{H}_{12}^+$) [35], 160 ($\text{PO}_2\text{NC}_5\text{H}_7^+$) [28], 143 ($\text{PO}_2\text{NC}_2\text{H}_7^+$) [45], 142 ($\text{PO}_2\text{NC}_5\text{H}_5^+$) [74], 79 ($\text{C}_5\text{H}_5\text{N}^+$) [100], 78 ($\text{C}_5\text{H}_4\text{N}^+$) [70]. Infrared spectrum (thin film, cm^{-1}): 2981 (m), 1387 (w), 1252 (s), 1237 (s), 989 (s), 768 (m), 538 (m). NMR spectra (27 °C): $^{31}\text{P}\{\text{H}\}$ (neat) δ 8.1; $^{13}\text{C}\{\text{H}\}$ (CDCl_3) δ 150.1 ($J_{\text{PC}} = 23.0$ Hz, C_6), 135.6 ($J_{\text{PC}} = 12.1$ Hz, C_4), 127.2 (C_3), 125.3 ($J_{\text{PC}} = 4.1$ Hz, C_5), 71.4 ($\text{CH}(\text{CH}_3)_2$), 23.7 (CH_3) (C_2 , unresolved).⁸

$[(i\text{-PrO})_2\text{P}(\text{O})\text{C}_5\text{H}_4\text{NO}]$ (**2**). Anal. Calcd for $\text{PO}_4\text{NC}_5\text{H}_8\text{O}$: C, 50.97; H, 7.00; N, 5.40. Found: C, 50.07; H, 7.23; N, 4.76. Mass spectrum [m/e (fragment) [relative intensity]]: 260 ($M + 1^+$) [12], 259 (M^+) [18], 200 ($\text{PO}_3\text{NC}_5\text{H}_{11}^+$) [51], 160 ($\text{PO}_3\text{NC}_5\text{H}_7^+$) [12], 158 ($\text{PO}_3\text{NC}_5\text{H}_5^+$) [16], 79 (NC_5H_7^+) [55], 78 (NC_5H_4^+) [100], 43 (C_3H_7^+) [61]. Infrared spectrum (thin film, cm^{-1}): 3443 (m), 2982 (s), 1424 (s), 1286 (s), 1258 (s), 992 (s), 773 (s), 587 (s). NMR spectra (27 °C): $^{31}\text{P}\{\text{H}\}$ (neat) δ 2.2; $^{13}\text{C}\{\text{H}\}$ (CDCl_3) δ 139.5 ($J_{\text{PC}} = 5.0$ Hz, C_6), 131.5 ($J_{\text{PC}} = 10.4$ Hz, C_4), 128.1 (C_5), 123.9 ($J_{\text{PC}} = 10.9$ Hz, C_3), 72.4 ($J_{\text{PC}} = 6.0$ Hz, $\text{CH}(\text{CH}_3)_2$), 72.3 ($J_{\text{PC}} = 5.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 23.5 (CH_3), C_2 , unresolved).

Preparation of $\text{La}(\text{NO}_3)_3 \cdot 2\text{-}[(i\text{-PrO})_2\text{P}(\text{O})\text{C}_5\text{H}_4\text{NO}]_2$ (5**).** The complex was prepared by addition of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.29 g, 0.9 mmol) in 10 mL of ethanol to **2** (0.48 g, 1.9 mmol) in 10 mL of ethanol. The solvent was allowed to slowly evaporate overnight; the resulting oil was washed with hexane and then redissolved in CHCl_3 . This solution was allowed to evaporate very slowly over several days, and a white crystalline product was obtained. The complex is soluble in CHCl_3 , CH_2Cl_2 , water, and THF. Anal. Calcd for $\text{LaP}_2\text{O}_{17}\text{N}_5\text{C}_{22}\text{H}_{36}$: C, 31.33; H, 4.30; N, 8.30. Found: C, 30.73; H, 4.45; N, 8.31. Infrared spectrum (KBr, cm^{-1}): 2986 (m), 1467 (s), 1459 (s), 1384 (s), 1301 (s), 1274 (m), 1229 (s), 1203 (s), 999 (s), 789 (m), 595 (m). NMR spectrum (27 °C): $^{31}\text{P}\{\text{H}\}$ (ethanol) δ 1.5.

X-ray Diffraction Study. Data were collected at 22 °C by variable $\theta-2\theta$ scans on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator and using Mo $\text{K}\alpha$ radiation. The structure was solved by Patterson and difference Fourier methods and refined to the

**Figure 1.** Molecular geometry and atom-labeling scheme for $\text{La}(\text{NO}_3)_3 \cdot 2\text{-}[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{C}_5\text{H}_4\text{NO}]_2$ (30% ellipsoids).**Scheme I**

observed data ($I \geq 2\sigma(I)$) with full-matrix least-squares methods using appropriate neutral-atom scattering factors and anomalous scattering terms.⁹ Refinements included anisotropic thermal parameters for all atoms heavier than hydrogen and a correction for secondary extinction.¹⁰ No attempt was made to locate hydrogen atoms. The Los Alamos crystal structure codes¹¹ 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 $\sigma(I) = \sigma_c(I) + (0.03I)^2$; $\sigma_c(I)$ is the error based on counting statistics. Lattice and data collection parameters are given in Table I. Coordinates and bond distances and bond angles are given in Tables II and III. An ORTEP projection of the complex and atom-numbering scheme are shown in Figure 1.

Results and Discussion

Syntheses for the 2-(diisopropoxyphosphino)pyridine *P*-oxide, $[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{C}_5\text{H}_4\text{N}]$ (**1**) and 2-(diisopropoxyphosphino)pyridine *N,P*-dioxide, $[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{C}_5\text{H}_4\text{NO}]$ (**2**) have not been previously reported. In the present study, these ligands were prepared in a manner similar to the respective routes established for the diethoxy analogues, $[(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{C}_5\text{H}_4\text{N}]$ (**3**) and $[(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{C}_5\text{H}_4\text{NO}]$ (**4**),⁷ and the synthetic procedure is outlined in the Scheme I. The yield of **1** from the present synthetic scheme is low; however, the oxidative conversion to **2**

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(8) The ring carbon atom numbering scheme is defined in ref 7.

Table II. Fractional Coordinates for $\text{La}(\text{NO}_3)_3[2\text{-}[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})]\text{C}_5\text{H}_4\text{NO}]_2$

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²	atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
La	0.0000 (0)	0.28246 (8)	0.25000 (0)	3.3	O1	0.0652 (3)	0.4525 (6)	0.3368 (2)	4.1
P1	0.1476 (1)	0.4497 (2)	0.3840 (1)	4.1	O2	0.1609 (4)	0.3448 (7)	0.4383 (2)	5.9
C1	0.0984 (6)	0.3173 (11)	0.4664 (4)	6.5	C2	0.1313 (9)	0.3846 (14)	0.5303 (5)	9.6
C3	0.0895 (9)	0.1570 (13)	0.4680 (6)	9.9	O3	0.1770 (4)	0.5996 (7)	0.4130 (3)	5.7
C4	0.1320 (6)	0.7342 (10)	0.3893 (5)	6.2	C5	0.0756 (9)	0.7601 (14)	0.4227 (8)	12.4
C6	0.1938 (8)	0.8516 (14)	0.3995 (7)	10.8	C7	0.2254 (5)	0.3937 (9)	0.3549 (3)	3.9
N1	0.2115 (4)	0.2674 (7)	0.3234 (3)	3.9	O4	0.1429 (3)	0.1974 (6)	0.3154 (3)	4.6
C8	0.2956 (5)	0.4716 (10)	0.3615 (4)	5.0	C9	0.3521 (6)	0.4192 (12)	0.3364 (5)	6.5
C10	0.3360 (6)	0.2872 (13)	0.3064 (5)	6.7	C11	0.2654 (5)	0.2102 (10)	0.2995 (4)	5.2
O5	0.0008 (4)	0.0247 (6)	0.2035 (3)	5.8	N2	0.0000 (0)	-0.0448 (13)	0.2500 (0)	5.0
O6	0.0000 (0)	-0.1763 (10)	0.2500 (0)	9.5	O7	0.0712 (4)	0.2562 (6)	0.1684 (3)	9.1
N3	0.1094 (5)	0.3736 (10)	0.1787 (4)	6.1	O8	0.1447 (6)	0.4156 (10)	0.1456 (4)	13.1
O9	0.1101 (4)	0.4453 (7)	0.2250 (3)	5.2					

^a(*U*₁₁ + *U*₂₂ + *U*₃₃)/3; anisotropic thermal parameters are published as supplementary data.

Table III. Selected Bond Distances and Angles for $\text{La}(\text{NO}_3)_3[2\text{-}[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})]\text{C}_5\text{H}_4\text{NO}]_2$

Distances (Å)			
La-O1	2.503 (5)	La-O4	2.545 (6)
La-O5	2.638 (6)	La-O7	2.622 (6)
La-O9	2.668 (6)	P1-C7	1.793 (8)
P1-O1	1.469 (5)	P1-O2	1.548 (6)
P1-O3	1.558 (6)	C1-C2	1.53 (1)
C1-C3	1.50 (2)	C1-O2	1.48 (1)
C4-C5	1.47 (2)	C4-C6	1.50 (1)
C4-O3	1.48 (1)	C7-C8	1.39 (1)
C7-N1	1.36 (1)	C8-C9	1.40 (1)
C9-C10	1.39 (1)	C10-C11	1.39 (1)
C11-N1	1.36 (1)	N1-O4	1.318 (8)
N2-O5	1.265 (8)	N2-O6	1.23 (1)
N3-O7	1.259 (9)	N3-O8	1.211 (9)
N3-O9	1.263 (9)		
Angles (deg)			
C7-P1-O1	113.1 (3)	C7-P1-O2	102.0 (4)
C7-P1-O3	104.3 (4)	O1-P1-O2	116.6 (3)
O1-P1-O3	113.1 (3)	O2-P1-O3	106.4 (4)
O5-N2-O5'	118 (1)	O5-N2-O6	120.8 (5)
O7-N3-O8	120.8 (9)	O7-N3-O9	118.0 (7)
O8-N3-O9	121.2 (9)		

is quantitative. The compounds have been characterized by elemental analyses, mass spectrometry, and infrared and NMR spectroscopy.

The phosphonate **1** displays a phosphoryl stretching frequency at 1252 cm⁻¹, which is comparable with ν_{PO} for **3**, 1253 cm⁻¹. The *N,P*-dioxide **2** displays bands at 1286 and 1258 cm⁻¹, which are assigned to ν_{NO} and ν_{PO} , respectively. The corresponding bands for **4** appear at 1284 and 1255 cm⁻¹. The ³¹P{¹H} and ¹³C{¹H} NMR spectra for **1** and **2** have been recorded and fully assigned. The ³¹P{¹H} NMR spectra each show a singlet: **1**, δ 8.1; **2**, δ 2.2. These resonances are similar to the shifts reported for **3** (δ 9.9) and **4** (δ 4.6). The ¹³C{¹H} NMR spectra compare very well between **1** and **3** and between **2** and **4** except that the expected widely spaced doublets for the C2 carbon in **1** and **2** were not detected.

The coordination chemistry of **2** with several lanthanides (La, Pr, Sm, Gd, Tb, Er) was examined; however, La(NO₃)₃ was the only salt that produced a crystalline complex. The remaining lanthanides formed oils which, to date, have resisted purification and crystallization. Combination of **2** with La(NO₃)₃·6H₂O in a 2:1 ratio provides a white crystalline solid shown to be La(NO₃)₃[2-[(*i*-C₃H₇O)₂P(O)]C₅H₄NO]₂ (**5**) by elemental analysis, spectroscopic data, and single-crystal X-ray diffraction analysis. The infrared spectrum of **5** shows a phosphoryl stretching frequency at 1203 cm⁻¹, downshifted 55 cm⁻¹ from ν_{PO} in the free ligand. This shift is similar to the shift, 69 cm⁻¹, observed upon coordination of **4** with UO₂(NO₃)₂.⁷ The ν_{NO} vibration in **5** is assigned to a band as 1229 cm⁻¹, and this represents a 57-cm⁻¹ shift from ν_{NO} in **2**. The corresponding *N*-oxide coordination shift for the uranyl complex is also reported to be 57 cm⁻¹. These frequency shifts are consistent with relatively strong interactions between the N-O and P-O coordination sites and the La(III) ion.¹²

The crystal structure determination for **5** confirms the bis-(ligand) stoichiometry assignment for the complex, and a view of the molecule is shown in Figure 1. The complex has 2-fold crystallographic symmetry. The ligands are bonded to the La(III) ion in a bidentate coordination mode, and the chelate rings have an approximately cyclohexane-like chain configuration. The La(III) ion is 10-coordinate with the coordination polyhedron composed of six oxygen atoms from three bidentate planar nitrate ions and four oxygen atoms from two bidentate ligands. The coordination condition is not accurately described by any regular polyhedron. The average La-O(nitrate) distance, 2.643 (6) Å (range 2.622 (6)–2.668 (2) Å), is identical with the average distance in La(NO₃)₃(dimethyl sulfoxide)₄, 2.65 ± 0.03 Å.¹⁵ The lanthanum bonded N-O(nitrate) average distance, 1.262 (9) Å (range 1.259 (9)–1.265 (8) Å), is longer, as expected, than the average noncoordinated N-O(nitrate) distance, 1.211 (9) Å. The La-O(phosphoryl) distance, 2.503 (5) Å, is comparable with the Sm-O(phosphoryl) distance, 2.418 (3) Å, found in the (carbamoylmethyl)phosphonate complex⁶ Sm(NO₃)₃[(C₃H₇O)₂P(O)-CH₂C(O)NEt₂]₂ when the difference in ionic radii for La(III) and Sm(III) is considered. In the latter complex, the CMP ligands are also bonded in a bidentate fashion to the Sm(III) ion. The lanthanum-bonded phosphoryl P-O distance in **5**, 1.469 (5) Å, may be compared with the P-O distances in UO₂(NO₃)₂[2-[(EtO)₂P(O)]C₅H₄NO], 1.46 (2) Å,⁷ and in Sm(NO₃)₃[(C₃H₇O)₂P(O)CH₂C(O)NEt₂]₂, 1.480 (2) Å. The La-O(*N*-oxide) distance in **5**, 2.545 (6) Å, is longer than the Sm-O(carbonyl) distance in Sm(NO₃)₃[(*i*-C₃H₇O)₂P(O)CH₂C(O)NEt₂]₂, 2.433 (2) Å, even when the difference in lanthanide radii is accounted for. Last, the N-O(*N*-oxide) distance in **5**, 1.318 (8) Å, may be compared with the N-O distance, 1.37 (2) Å, in UO₂(NO₃)₂[2-[(EtO)₂P(O)]C₅H₄NO].

This work and our earlier studies⁷ indicate that the bifunctional ligand **2** forms complexes with La(III) and UO₂²⁺ that are structurally related to early lanthanide and uranyl complexes with (carbamoylmethyl)phosphonates. Although numerous other features eventually contribute to, and determine, the suitability of a ligand class as a liquid-liquid extractant, it appears that there is no structural feature that should prevent the 2-(dialkoxyphosphino)pyridine *N,P*-dioxides from acting as good Ln(III) ion extractants. In fact, phosphoryl and *N*-oxide distances in **5** are consistent with a stronger ligand-metal interaction in the La(III) complex compared to the *N,P*-dioxide ligand interaction in the

- (12) It is noted that the assignments of the coordinated ν_{NO} and ν_{PO} bands in **5** are not unambiguous. It is possible that the assignments for these closely spaced bands may be reversed. If this is the case, then the coordination shifts are $\Delta\nu_{\text{NO}} = 83 \text{ cm}^{-1}$ and $\Delta\nu_{\text{PO}} = 29 \text{ cm}^{-1}$. The N-O coordination shift is not unreasonable as noted by Karayannis and co-workers;¹³ however, the phosphoryl shift would be smaller than typically found in coordination complexes of bifunctional phosphonate ligands.^{6,7,14}
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related uranyl complex. Liquid–liquid extraction studies are in progress that will provide a quantitative evaluation of the separation capabilities of the ligands.

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Supplementary Material Available: Table SI, listing thermal parameters (2 pages); Table SII, listing observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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⁹⁹Tc NMR Spectroscopy of Technetium(I) Phosphine and Phosphite Complexes

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The recent increased interest in the chemistry of technetium, due to its widespread use in nuclear medicine, has led us to investigate the use of ⁹⁹Tc NMR spectroscopy as a tool for the identification of technetium complexes. ⁹⁹Tc, which is obtained free from isotopic contamination, has a nuclear spin of 9/2 and a very high receptivity relative to ¹H of 0.275. The standard reference sample for this isotope is taken as (NH₄)[TcO₄] in D₂O which resonates² with $\delta = 22\,508\,304$. We have studied a range of diamagnetic complexes with technetium in the oxidation states +1 to +7, but in this brief note we wish to report some of our studies on technetium(I) complexes since it appears that erroneous data may have appeared recently.

Experimental Section

Caution! ⁹⁹Tc is a β^- emitter ($t_{1/2} = 2.1 \times 10^5$ years). All manipulations of solutions and solids were performed in a laboratory approved for the handling of radioisotopes using precautions outlined elsewhere.³

The complexes [Tc(dmpe)₃](PF₆)⁴ and [Tc(P(OMe)₃)₆](BPh₄)⁵ were prepared by literature methods. Ammonium pertechnetate was supplied as a gift by DuPont Biomedical Products.

⁹⁹Tc NMR spectra were recorded at 23 °C on a Varian XL-300 instrument with a 7.05-T superconducting magnet. A 34- μ s pulse width (90° tip) and 0.15-s acquisition time were used. No additional relaxation delay was used unless TcO₄⁻ ($T_1 = 0.1$ s)^{2,6} was present. The spectral width was set at 10⁵ Hz by using 30016 data points in the FID weighted with 10-Hz Gaussian line broadening. The reference sample ((NH₄)[⁹⁹TcO₄] in D₂O = 0 ppm) resonates at 67.516 MHz in this spectrometer. For differences greater than the maximum spectral width (10⁵ Hz, 1480 ppm) obtainable, chemical shifts could be calculated manually based on the spectrometer frequency, transmitter offset, transmitter base offset, and relative shift within the spectral window. We estimate that the error associated with these values is $\sim \pm 2$ ppm.

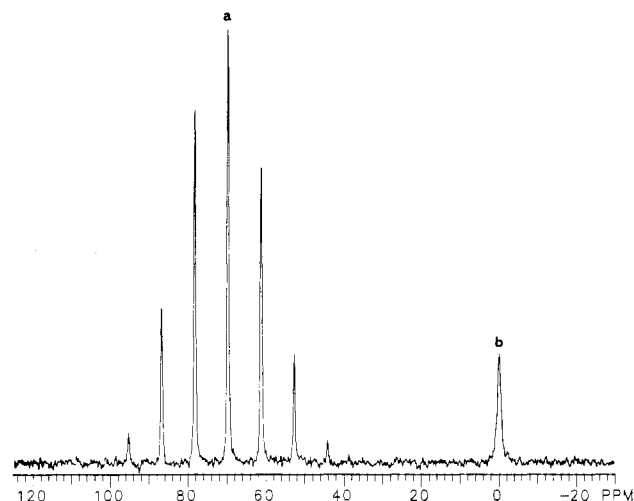


Figure 1. ⁹⁹Tc NMR spectrum of a mixed sample containing (a) [Tc(dmpe)₃](PF₆) and (b) [Tc(CNBU₆)₆](PF₆) in CDCl₃ showing the proximity of their chemical shifts. The chemical shift of [Tc(CNBU₆)₆]⁺ (-1914 ppm) is arbitrarily set to 0 ppm.

The absence of spectral folding or other artifacts was ruled out by changing the transmitter offset by a known frequency and verifying that the resonance moved within the spectral window by the appropriate amount and in the expected direction. For example, decreasing the transmitter offset by 10000 Hz should lead to a relative positive chemical shift of ~ 150 ppm.

Results and Discussion

The known chemical shifts for technetium complexes range from +2800 ppm for the *trans*-dioxotetrakis(pyridine)technetium(V) cation to -3672 ppm for the nonahydridotechnetate(VII) dianion, relative to that for ammonium pertechnetate(VII), 0 ppm. The former has been determined in our laboratory while the resonance of TcH₂²⁺ was reported by Lock,⁶ who also first measured the resonance of a Tc(I) complex, [Tc(CNBU₆)₆]⁺, at -1902 ppm. We have remeasured this compound with several different spectrometers and find its resonance in good agreement with that previously reported, coming at -1914 ppm. Spectra of more than 20 different analogues with substituted isocyanides have been measured, and all fall within ± 50 ppm of the *tert*-butyl derivative. Recently, Lorenz and co-workers⁷ have measured the resonances of Tc₂(CO)₁₀, a spin-paired Tc(0) species, and the Tc(I) carbonyl complexes Tc(CO)₅Br and TcCl(CO)₃(PPh₃)₂. The shift of the first is at -2477 ppm while those for the others occur at -1630 and -1488 ppm, respectively.

The basic spectral range may be readily understood in terms of the Griffith and Orgel theory,⁸ which relates chemical shifts to the ΔE between HOMO and LUMO. Our technetium study correlates well with the observations for ⁹⁵Mo NMR spectroscopy,⁹ in which MoO₄²⁻ appears near the center of the chemical shift range while Mo(CO)₆ is at -2000 ppm relative to the molybdate reference. The chemical shifts for molybdenum(0) complexes, -1000 to -2120 ppm, agree well with our observations for the isoelectronic technetium(I) species. Additionally, it is known that d² molybdenum(IV) species are heavily deshielded and the shifts occur at lower field than those for molybdate. Similarly, the technetium(V) species that we have studied have resonances downfield from pertechnetate.

We were surprised, therefore, that two other groups reported^{4,10} that the resonance of the technetium(I) complex [Tc(dmpe)₃]⁺ (dmpe = 1,2-bis(dimethylphosphino)ethane) occurred at -13 ppm

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