spectively. The boron atom for each of these BF_4^- groups was placed at coordinates calculated by averaging the corresponding fluorine coordinates. These coordinates were not refined but were recalculated periodically (final boron-boron separation = 0.50 Å). The isotropic temperature factors for the boron atoms were refined. The populations for the groups refined to final values of 0.71 and 0.29.

The final refinement of the structure was done by block-diagonal least-squares with two matrices. All nonhydrogen positional parameters were included in one matrix; the second contained all nonhydrogen thermal parameters, the BF_4^- population factor, and the scale factor. No reflections were omitted from this refinement. The final R was 0.051 for the 665 reflections with $F_o^2 > 3\sigma$ and 0.143 for all data. The goodness of fit $[\sum w(F_o^2 - F_c^2)^2/(m-s)]^{1/2}$ was 1.19, where $m = 1941$ is the number of observations and $s = 209$ is the number of parameters. Features on a final difference map were between −1.4 e/Å^3 (at the position of Cu) and 1.2 e/Å^3 (near F4A). Final atomic parameters are given in Tables III and IV.

Crystallographic Characterization of $Cu_2(TPEN)(CO)_2(BF_4)_2$ (2). An approximately cubic crystal, 0.2 mm on an edge, was sealed in epoxy to prevent decomposition and was used for all X-ray diffraction measurements. Preliminary oscillation and Weissenberg photographs showed Laue symmetry $2/m$ with systematic absences $h0l$ with l odd and $0k0$ with k odd, indicating the monoclinic space group $P2_1/c$; the crystal was then transferred to a Syntex P2$_1$ diffractometer operating with Ni-filtered Cu Kα radiation. Unit cell dimensions were obtained by centering 15 well-scattered reflections with 2θ values ranging from 23 to 48°. Intensities were measured with use of a θ–2θ scan at a rate of 2°/min with an equal amount of time spent on backgrounds; three check reflections, monitored every 100 measurements, showed no intensity decay or abnormal fluctuations. All reflections out to $2\theta = 100°$ were measured in two different quadrants ($\pm h,k,l$ and $\pm h,-k,-l$) and were averaged to yield 3558 net intensities, of which 2998 were greater than zero.

The initial attempt at solving the structure was by manual application of direct methods based on 95 reflections with $|E|$ greater than 1.85, three origin-fixing signs, and two symbolic signs. The resulting E map was not structurally reasonable because, as it turned out, one of the early sign entries was reversed. A three-dimensional Patterson map was then calculated and quickly led to the positions of the Cu atoms. The C, N, O, B, and F atoms were recovered from F_o and difference maps; the positions of the hydrogen atoms were calculated with use of a C–H bond length of 0.9 Å. In the least-squares refinement the same quantity was minimized as in the preceding structure, with weights calculated in the same manner.

A late difference map indicated rather severe disorder for one of the BF_4^- groups: while three of the fluorine atoms could be adequately represented by large, anisotropic B's, the fourth could not and accordingly was split into two half-occupied sites separated by about 1.2 Å.

In the final least-squares cycles, three matrices were collected, each of order between 140 and 150: the coordinates of the 49 nonhydrogen atoms in one, anisotropic B's for half the cation and one of the BF_4^- groups in a second, and anisotropic B's of the remaining atoms, a scale factor, and an extinction parameter in the third. The final value of the goodness of fit was 1.87 for the 3558 measured reflections; the R factors were 0.062 for the 2998 reflections with net intensity greater than zero and 0.042 for the 2271 reflections with intensities greater than 3 esd's above background. Features on a difference map were between −0.8 and 0.6 e/Å^3, in generally uninteresting places.

All calculations were carried out on the CRYM system of programs. Final atomic parameters are given in Tables III and IV, on the basis of the numbering scheme shown in Figure 4.

Acknowledgment. We appreciate helpful discussions with Grant A. Mauk and financial assistance from the National Institutes of Health (Grant No. PHS AM18319), the International Copper Research Association, and a Sloan Fellowship (to R.R.G.).

Registry No. **1**, 79483-34-4; **2**, 79483-36-6; $Cu(CH_3CN)_4BF_4$, 15418-29-8.

Supplementary Material Available: Listings of the observed and calculated structure factors for $Cu_2(TPEN)(BF_4)_2$ and $Cu_2(TPEN)(CO)_2(BF_4)_2$ (22 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal and Molecular Structure of a [Diethyl (*N*,*N*-diethylcarbamyl)methylenephosphonate]thorium Nitrate Complex

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[Diethyl (*N*,*N*-diethylcarbamyl)methylenephosphonate]thorium(IV) nitrate, $Th[(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2]_2(NO_3)_4$ (**1**), has been prepared from the combination of an acidic solution of $Th(NO_3)_4$ and a benzene solution of the carbamyl phosphonate ligand. The resulting complex has been characterized by infrared and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopies. A single-crystal X-ray analysis of **1** has been completed, and the complex was found to crystallize in the monoclinic space group $C2/c$ with $a = 20.754$ (6) Å, $b = 8.470$ (1) Å, $c = 21.183$ (5) Å, $\beta = 101.69$ (2)°, $Z = 4$, $V = 3646.6$ Å^3, and $\rho_{calcd} = 1.79$ g cm^{-3}. The structure was solved by standard heavy-atom techniques. Full-matrix least-squares refinement of the structure has led to final discrepancy indices of $R_F = 4.0\%$ and $R_{wF} = 5.0\%$ on the basis of 4385 independent reflections. The crystal contains monomeric units of **1** that have crystallographic C_2 symmetry. The thorium atom is bonded to both carbonyl and phosphoryl oxygen atoms of two carbamyl phosphonate ligands and two oxygen atoms of each of four nitrate groups. The resulting coordination number for the thorium atom is 12. Several important bond distances include Th–O(carbonyl) 2.453 (4) Å, Th–O(phosphoryl) 2.482 (4) Å, and Th–O(nitrate) 2.638 (3) Å (average).

Introduction

Siddall and co-workers[1-3] and more recently Petrzilova[4] and Schulz and McIsaac[5] have studied the extraction chemistry of carbamylmethylenephosphonate (CMP) ligands with a number of lanthanide and actinide ions found in liquid, acidic, radioactive waste. Primarily on the basis of equilibrium distribution measurements, it has been concluded that trivalent lanthanide and actinide ions form tris-chelate complexes, $M(CMP)_3^{3+}$, in which the metal ion is bonded to the CMP ligands in a bidentate coordination mode through the carbonyl and phosphoryl oxygen atoms.[1-5] Some limited infrared spectroscopic data appear to support the structural assumption;[3,6] however, unambiguous stoichiometry and structure

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(1) Siddall, T. H. *J. Inorg. Nucl. Chem.* **1963**, *25*, 883.
(2) Siddall, T. H. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1991.
(3) Stewart, W. E.; Siddall, T. H. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3599.
(4) Petrzilova, H.; Binka, J.; Kuca, L. *J. Radioanal. Chem.* **1979**, *51*, 107.
(5) Schulz, W. W.; McIsaac, L. D. "Transplutonium Elements"; Müller, W., Lindmer, R. Eds.; North-Holland Publishing Co.: Amsterdam, 1976; p 433.
(6) Stewart, W. E.; Siddall, T. H. *J. Inorg. Nucl. Chem.* **1968**, *30*, 3281.

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assignments for a tervalent complex have not been reported.[7] The stoichiometry and structures for tetravalent actinide–CMP complexes have not been fully determined, and the nature of the extraction chemistry involving tetravalent actinide ions is not well understood.

We have recently observed that CMP ligands are readily deprotonated at the methylene carbon atom spanning the phosphoryl and carbonyl functional groups.[8] Further, mercury(II) readily bonds to the methine carbon atom[9] of the anionic form of the ligand. This observation and the uncertainties described above have led us to more carefully examine the bonding displayed between CMP ligands and lanthanide and actinide ions under a variety of conditions. We report here the synthesis, isolation, and spectroscopic characterization of a complex formed in acidic solution from the combination of Th(IV) and a CMP ligand. The structure of the resulting complex, $Th[(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2]_2(NO_3)_4$ (**1**), also has been determined by using single-crystal X-ray diffraction methods.

Experimental Section

General Information. $(CH_3CH_2O)_2P(O)CH_2C(O)N(C_2H_5)_2$, DEDECMP, was prepared by literature methods,[1] and thorium nitrate was obtained from Ventron Corp. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer using KBr pellets. NMR spectra were recorded on a Varian XL-100 NMR spectrometer operating at 25.2 MHz (^{13}C) and 40.5 MHz (^{31}P) and a Varian FT-80 NMR spectrometer operating at 80.0 MHz (^{1}H) and 20.0 MHz (^{13}C). Samples were contained in 5-mm tubes rigidly held in a 12-mm tube containing a deuterated lock solvent when the XL-100 NMR spectrometer was used. An internal deuterium lock was used in 5-mm tubes on the FT-80 spectrometer. Spectral standards were $(CH_3)_4Si$ (^{13}C, ^{1}H) and 85% H_3PO_4 (^{31}P).

Preparation of $Th(DEDECMP)_2(NO_3)_4$ (1). A 50-mL sample of a solution of 1 M $Th(NO_3)_4$ in 1 M HNO_3 was added to 40 mL of a solution containing 38.6 mmol of $(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2$ in benzene. A colorless precipitate formed at the interface immediately upon combination. The mixture was placed in a sealed bottle and shaken overnight. The solid product was recovered by filtration, washed quickly with water and benzene, and dried in vacuo. The product is partially soluble in water, acetone, and acetonitrile. Recrystallization from water gave crystals suitable for single-crystal X-ray analysis. Anal. Calcd for $ThC_{20}O_{20}N_6P_2H_{44}$: C, 24.4; H, 4.51; O, 32.6; N, 8.54; P, 6.30; Th, 23.6. Found: C, 23.6; H, 3.91; O, 34.6; N, 8.59; P, 5.87; Th, 23.0. Infrared spectrum (cm^{-1}) (KBr pellet): 2985 (m), 2938 (m), 2539 (w), 2287 (w), 1591 (ν_{CO}, s), 1487 (br, s), 1284 (br, s), 1156 (ν_{PO}, s) 1024 (ν_{POC}, s), 956 (m), 806 (m), 738 (s), 679 (m), 624 (m), 437 (m), 214 (br, s). NMR spectra (CH_3CN solvent, 27 °C): $^{31}P\{^1H\}$ δ 27.68; $^{13}C\{^1H\}$ δ 167.7 ($^2J_{PC(2)} = 8.3$ Hz), 65.8 ($^2J_{PC(7)} = 7.1$ Hz), 44.3, 42.7, 15.4, 15.1, 13.0, 11.6; ^1H δ 4.08 ($^3J_{PH} = 7.1$ Hz), 3.32, 2.54 ($^2J_{PH} = 19.9$ Hz), 1.15.

Crystal Structure Determination. A suitable crystal (0.36 mm × 0.11 mm × 0.34 mm) was sealed in a glass capillary. The crystal was centered on a Syntex P3/F automated diffractometer, and the determinations of the crystal class, orientation matrix and accurate unit cell dimensions were performed in a standard manner.[10] The data were collected at 298 K by the θ–2θ technique using Mo Kα radiation, a scintillation counter, and a pulse-height analyzer. A summary of the data collection parameters appears in Table I. Inspection of the data revealed systematic absences $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$, consistent with the monoclinic space group $C2/c$ and its noncentric counterpart Cc. Corrections for absorption were made on the basis of a series of eight ψ scans. The redundant and equivalent reflection data were averaged and converted to $|F_o|$ values following corrections for Lorentz and polarization effects.

Table I. Experimental Data for the X-ray Diffraction Study of $Th[(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2]_2(NO_3)_4$

(A) Crystal Parameters at 25 °C

crystal system: monoclinic	$V = 3646.6$ Å^3
space group: $C2/c$	$Z = 4$
$a = 20.754$ (6) Å	mol wt = 982.6
$b = 8.470$ (1) Å	$F(000) = 2544$
$c = 21.183$ (5) Å	$\rho_{(calcd)} = 1.79$ g cm^{-3}
$\beta = 101.69$ (2)°	$\rho_{(obsd)} = 1.73$ g cm^{-3}

(B) Measurement of Intensity Data

diffractometer: Syntex P 3/F
radiation: Mo Kα ($\bar{\lambda} = 0.71069$ Å)
monochromator: highly oriented graphite crystal
reflctns measd: $+h,+k,\pm l$
2θ range: 1–60°
scan type: θ–2θ
scan speed: 4.0–30.0°/min
scan range: from $[2\theta(K\alpha_1) - 1.0]°$ to $[2\theta(K\alpha_2) + 1.0]°$
bkgd measmt: stationary crystal, stationary counter; at beginning and end of 2θ scan—each for half the time taken for 2θ scan
standard reflections: 2 measured every 48 reflections [400, 023]; no significant changes in intensity observed
reflctns collctd: 5481 total, yielding 5350 independent reflections
reflctns obsd ($I \geqslant 1.96\sigma_I$): 4385 (82%)
abs coeff: 44.0 cm^{-1}; empirical absorption correction made on the basis of ψ scans

Solution and Refinement of the Structure. All calculations were performed on a Syntex R3/XTL structure determination system. The scattering factor for Th was taken from Roof.[11] Scattering factors for the P, O, N, and C atoms were taken from the compilation of Cromer and Waber[12] while those for hydrogen were taken from the listing of Stewart and co-workers.[13] Both real ($\Delta f'$) and imaginary ($\Delta f''$) components of the anomalous dispersion were included for the nonhydrogen atoms with use of the values listed by Cromer and Liberman.[14] The function minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$.

The solution and refinement of the structure were based on 4385 reflections with $I \geq 1.96\sigma_I$. The thorium atom was located on the crystallographic C_2 axis at 0, 0.15, 0.25 by using Patterson methods in space group $C2/c$, and subsequent Fourier synthesis revealed the locations of all remaining nonhydrogen atoms. Refinement of the positional and individual isotropic thermal parameters of the nonhydrogen atoms by means of a block-diagonal least-squares procedure gave convergence at $R_F = 7.4\%$.[15] Individual anisotropic thermal parameters were then applied for all nonhydrogen atoms. Refinement by a block-diagonalized least-squares procedure using counterweights, where $w = [\sigma_F^2 + (CF_o)^2]^{-1}$ with $C = 0.040$, gave convergence at $R_F = 4.4\%$. The positions of the methyl hydrogen atoms were then found by means of a difference Fourier synthesis, and the final positions were idealized with appropriate bond angles and distances.

A full-matrix least-squares refinement gave final discrepancy indices of $R_F = 4.0\%$ and $R_{wF} = 5.0\%$. A final difference Fourier synthesis revealed no unusual features and no peaks greater than 1.25 e Å^{-3}. A table of observed and calculated structure factor amplitudes is available in the supplementary data (Table S-1). Positional parameters are presented in Table II, and thermal parameters are available in the supplementary data (Table S-2).

Results and Discussion

The combination of $(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2$ (DEDECMP) in benzene solution with $Th(NO_3)_4$ in 1 M HNO_3 solution results in the formation of a colorless crystalline

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(7) Analytical data[3] are consistent with bis-chelate formulations; however, other supporting data have not been reported.

(8) Bowen, S. M.; Paine, R. T., to be submitted for publication.

(9) Bowen, S. M.; Duesler, E. N.; Paine, R. T.; Campana, C. F., submitted for publication.

(10) The hardware configuration for the P3/F diffractometer and the R3/XTL system has been described: Campana, C. F.; Sheppard, D. F.; Litchman, W. M. *Inorg. Chem.* **1981**, *20*, 4039. Programs used for centering reflections, autoindexing, refinement of cell parameters, axial photographs, full-matrix least-squares refinements, bond length and bond angle calculations, error analysis, least-squares plane calculations, direct-methods structure solutions, and calculation of hydrogen atom positions are those described in: "Syntex R3 Operations Manul"; R. A. Sparks, Ed.; Syntex Analytical Instruments: Cupertino, CA, 1978.

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(13) Stewart, R. F.; Davidson, R. F.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(14) Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970** *53*, 1891.

(15) Discrepancy indices used in the text are defined as follows: R_F (%) = $[\sum||F_o| - |F_c||/\sum|F_o| \times 100$, R_{wF} (%) = $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} \times 100$.

Table II. Positional Parameters and Their Esd's for $Th[(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2]_2(NO_3)_4$

atom	*x/a*	*y/b*	*z/c*
Th	0.0000 (0)	0.1483 (3)	0.2500 (0)
P(1)	0.1284 (1)	−0.1418 (2)	0.3266 (1)
O(1)	0.1044 (2)	0.0086 (4)	0.2949 (2)
O(2)	0.1679 (2)	−0.1212 (5)	0.3968 (2)
O(3)	0.1726 (2)	−0.2265 (6)	0.2866 (2)
O(4)	−0.0201 (2)	−0.0808 (4)	0.3141 (2)
O(5)	0.0942 (2)	0.2112 (5)	0.1915 (2)
O(6)	0.0356 (2)	0.4154 (5)	0.2013 (2)
O(7)	0.1183 (3)	0.4342 (7)	0.1526 (3)
O(8)	0.0375 (2)	0.1848 (5)	0.3764 (2)
O(9)	0.0941 (2)	0.3239 (5)	0.3225 (2)
O(10)	0.1118 (3)	0.3438 (7)	0.4266 (3)
N(1)	−0.0137 (3)	−0.2129 (6)	0.4065 (2)
N(2)	0.0834 (3)	0.3572 (6)	0.1804 (3)
N(3)	0.0823 (3)	0.2858 (7)	0.3764 (3)
C(1)	0.0641 (3)	−0.2748 (6)	0.3357 (3)
C(2)	0.0069 (3)	−0.1856 (6)	0.3525 (3)
C(3)	−0.0674 (4)	−0.1176 (7)	0.4223 (3)
C(4)	−0.1341 (5)	−0.1926 (13)	0.3964 (5)
C(5)	0.0109 (4)	−0.3407 (7)	0.4520 (3)
C(6)	0.0703 (5)	−0.2944 (11)	0.5014 (4)
C(7)	0.2207 (5)	−0.0042 (10)	0.4132 (4)
C(8)	0.2443 (7)	0.0018 (17)	0.4793 (6)
C(9)	0.2129 (6)	−0.3647 (11)	0.3104 (7)
C(10)	0.2487 (5)	−0.4132 (15)	0.2647 (7)
HC(11)	0.0491	0.6678	0.2953
HC(12)	0.0810	0.6502	0.3704
HC(31)	−0.0612	−0.1082	0.4692
HC(32)	−0.0664	−0.0124	0.4032
HC(41)	−0.1607	−0.1429	0.4286
HC(42)	−0.1326	−0.3086	0.3991
HC(43)	−0.1522	−0.1620	0.3514
HC(51)	−0.0242	−0.3711	0.4744
HC(52)	0.0224	−0.4310	0.4276
HC(61)	0.1071	−0.2857	0.4821
HC(62)	0.0789	−0.3748	0.5354
HC(63)	0.0622	−0.1924	0.5204
HC(71)	0.2574	−0.0349	0.3921
HC(72)	0.2044	0.0994	0.3970
HC(81)	0.2819	0.0762	0.5004
HC(82)	0.2577	−0.1049	0.4937
HC(83)	0.2059	0.0325	0.4983
HC(91)	0.2438	−0.3367	0.3507
HC(92)	0.1846	−0.4510	0.3192
HC(101)	0.2700	−0.3184	0.2509
HC(102)	0.2167	−0.4536	0.2271
HC(103)	0.2857	−0.5000	0.2768

solid, **1**, at the solvent (H_2O/benzene) interface. The recovered solid is partially soluble in water, acetone, and acetonitrile. Elemental analyses are most consistent with a molecular formula containing two DEDECMP ligands and four nitrate groups about the thorium atom, and the chemistry can be summarized by the equation

$$2(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2 + Th(NO_3)_4 \xrightarrow{H_2O/\text{benzene}} \underset{\mathbf{1}}{Th[(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2]_2(NO_3)_4}$$

The infrared spectrum for **1** recorded from a KBr pellet is similar to the spectra reported by Stewart and Siddall[3] for several CMP–lanthanide complexes of the general type M-$[(i\text{-PrO})_2P(O)CH_2C(O)NEt_2]_2(NO_3)_3$ (**2**). The band in **1** at 1591 cm^{-1} can be assigned to a carbonyl stretch shifted to lower frequency than the corresponding band at 1651 cm^{-1} in the free DEDECMP ligand. The band in **1** also appears at the low end of a region, 1617–1589 cm^{-1}, associated with ν_{CO} in the lanthanide complexes, **2**. The low-frequency shift upon coordination of the CMP ligand has been suggested to be diagnostic of metal ion-carbonyl oxygen atom bonding. The ν_{CO} band in **1** does not display the doublet structure found in several examples of **2**.[16] The band at 1156 cm^{-1} in **1** can be assigned to a phosphoryl band, ν_{PO}. In DEDECMP this band appears at 1264 cm^{-1}, and in **2** ν_{PO} falls in the region 1208–1201 cm^{-1}. The large low-frequency shift of ν_{PO} in **1** suggests a strong interaction between the thorium atom and the phosphoryl oxygen atom. Lastly, the band in **1** at 1024 cm^{-1} can be tentatively assigned to ν_{POC}, and this frequency is shifted up from the corresponding band in the free ligand at 969 cm^{-1}.

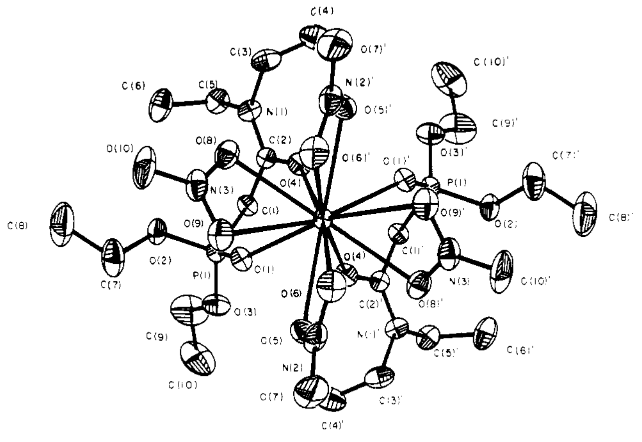

Figure 1. Molecular geometry and labeling scheme in $Th[(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2]_2(NO_3)_4$ (50% probability ellipsoids).

The NMR spectra of **1** warrant brief description. The $^{31}P\{^1H\}$ spectrum shows a singlet, 27.7 ppm, downfield from H_3PO_4. This resonance appears slightly downfield from the resonance in neutral DEDECMP, 23.7 ppm, slightly upfield from the resonance in $Hg(DEDECMP^-)(NO_3)$, 30.97 ppm,[9,17] and upfield from the resonances in $Na(DEDECMP^-)$, 45.3 ppm.[9] In $Na(DEDECMP^-)$, a proton has been removed from the methylene group bridging the P=O and C=O functions in the neutral ligand, which leaves an sp^2 carbon atom adjacent to the phosphorus atom. The mercury complex is dimeric with the mercury atom bonded to the deprotonated central carbon atom, which once again can be considered to be sp^3 hybridized.[9] However, the same Hg atom is also bonded in a bidentate fashion to the carbonyl and phosphoryl oxygen atoms of a second molecule of $Hg(DEDECMP^-)(NO_3)$. On the basis of these observations, the chemical shift for **1** is consistent with but does not demand a bidentate CMP ligand coordination with the central thorium atom.

The ^1H and $^{13}C\{^1H\}$ NMR spectra for **1** show resonances that can be directly assigned to the protons and carbon atoms in the phosphite and amide alkyl chains.[17] The bridging methylene group in DEDECMP appears at δ 2.89 (J_{PCH} = 21.9 Hz) in the ^1H spectrum and δ 34.05 (J_{PC} = 132.3 Hz) in the $^{13}C\{^1H\}$ spectrum. The ^1H spectrum for **1** compares favorably, δ 2.54 (J_{PCH} = 19.9 Hz); however, a ^{13}C resonance for the methylene carbon atom is not resolved. This unexpected result was also found in the $^{13}C\{^1H\}$ spectrum recorded for $[Hg(DEDECMP^-)NO_3]_2$.[9,18] Consequently, on the basis of these data, participation of the CMP bridging carbon atom in the bonding cannot be ruled out. So that the structure of

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(16) The ν_{CO} doublet observed in the infrared spectra of several lanthanide–CMP complexes was originally ascribed to the presence of bonded and nonbonded carbonyl functions;[6] however, this interpretation was later cast in doubt by additional studies.[3]

(17) The NMR spectra for DEDECMP show resonances as follows: ^1H, δ 2.89 (J_{PCH} = 21.9 Hz, CH_2 bridge), 3.94 (J_{OCH} = 7.2 Hz, OCH_2), 3.24 (NCH_2), 0.94–1.23 (CH_3), $^{13}C\{^1H\}$, δ 34.05 (J_{PC} = 132.3 Hz, CH_2 bridge), 164.3 (C=O), 62.62 (OCH_2), 17.04 (OCH_2CH_3), 42.16 (NCH_2), 14.2 (NCH_2CH_3).

(18) The ^1H and $^{13}C\{^1H\}$ NMR spectra for $Th[(i\text{-PrO})_2P(O)CH_2C(O)NEt_2]_2(NO_3)_4$ show resonances that can be assigned to the methylene protons and carbon atom: ^1H, δ 2.77 (J_{PCH} = 29.5 Hz); $^{13}C\{^1H\}$, δ 30.46 (J_{PC} = 141.2 Hz).

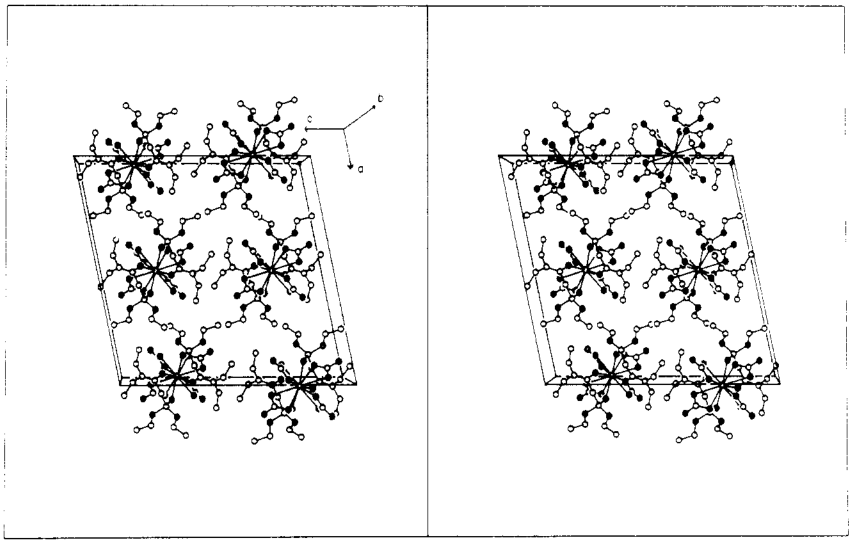

Figure 2. Stereoview of the molecular packing diagram for $Th[(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2]_2(NO_3)_4$.

Table III. Selected Interatomic Bond Distances (Å)

Th-O(1)	2.482 (4)	C(1)-C(2)	1.509 (8)
Th-O(4)	2.453 (4)	C(2)-O(4)	1.256 (6)
Th-O(5)	2.573 (4)	C(2)-N(1)	1.321 (7)
Th-O(6)	2.653 (5)	C(3)-N(1)	1.468 (9)
Th-O(8)	2.650 (4)	C(5)-N(1)	1.470 (8)
Th-O(9)	2.678 (5)	C(3)-C(4)	1.520 (13)
P(1)-O(1)	1.478 (4)	C(5)-C(6)	1.497 (12)
P(1)-O(2)	1.559 (5)	N(2)-O(5)	1.270 (7)
P(1)-O(3)	1.545 (5)	N(2)-O(6)	1.265 (8)
P(1)-C(1)	1.787 (6)	N(2)-O(7)	1.213 (8)
O(2)-C(7)	1.465 (10)	N(3)-O(8)	1.263 (8)
O(3)-C(9)	1.467 (12)	N(3)-O(9)	1.256 (7)
C(7)-C(8)	1.389 (15)	N(3)-O(10)	1.219 (8)
C(9)-C(10)	1.396 (19)		

Table IV. Selected Interatomic Bond Angles (Deg)

O(1)-Th-O(4)	69.1 (1)	O(1)-P(1)-O(3)	109.6 (3)
O(8)-Th-O(9)	47.5 (1)	O(2)-P(1)-O(3)	108.6 (3)
O(5)-Th-O(6)	48.5 (1)	O(1)-P(1)-C(1)	113.7 (2)
O(5)-Th-O(1)	66.1 (1)	O(2)-P(1)-C(1)	103.1 (3)
O(6)-Th-O(1)	105.4 (1)	O(3)-P(1)-C(1)	107.9 (3)
O(5)-Th-O(4)	131.4 (1)	O(4)-C(2)-C(1)	118.1 (5)
O(6)-Th-O(4)	169.2 (1)	N(1)-C(2)-O(4)	120.3 (5)
O(5)-Th-O(8)	111.5 (1)	N(1)-C(2)-C(1)	121.6 (5)
O(6)-Th-O(8)	104.2 (1)	P(1)-C(1)-C(2)	110.5 (4)
O(5)-Th-O(9)	68.0 (1)	O(5)-N(2)-O(6)	115.9 (5)
O(6)-Th-O(9)	61.4 (1)	O(5)-N(2)-O(7)	120.9 (6)
O(1)-Th-O(1')	123.0 (1)	O(6)-N(2)-O(7)	123.2 (6)
Th-O(4)-C(2)	144.5 (4)	O(8)-N(3)-O(9)	116.9 (5)
Th-O(1)-P(1)	140.6 (2)	O(8)-N(3)-O(10)	120.8 (6)
O(1)-P(1)-O(2)	113.6 (2)	O(9)-N(3)-O(10)	122.2 (6)

1 could be assigned with confidence, a single-crystal X-ray analysis was undertaken.

The results of the single-crystal X-ray structure determination indicate that the correct formulation for **1** is $Th[(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2]_2(NO_3)_4$. The structure contains discrete monomeric molecules having C_2 symmetry, and there are four molecules per unit cell. A view of the molecular unit is shown in Figure 1, and the molecular packing is illustrated in Figure 2. Selected interatomic bond distances and angles are summarized in Tables III and IV.

The central thorium atom is bonded to two bidentate, neutral DEDECMP ligands and four bidentate nitrate ions. The thorium–phosphoryl oxygen atom bond distance, Th–O(1) 2.482 (4) Å, is longer than the average Th–O(phosphoryl) bond distances in $Th[OP(C_6H_5)_3]_2(NO_3)_4$[19] (**3**), 2.35 (2) Å, tetrakis[1,1,1-trifluoro-3-(2-thenoyl)acetonato](tri-*n*-octylphosphine oxide)thorium(IV)[20] (**4**), 2.30 Å, $[Th(NO_3)_3\{OP(CH_3)_3\}_4]_2[Th(NO_3)_6]$[21] (**5**) 2.34 Å, and $[Ph_4P][Th\{OP(CH_3)_3\}_2(NO_3)_5]$[21] (**6**), 2.38 Å, yet the Th–O(1) distance falls within the upper end of the ranges of Th–O bond distances found in several of these compounds. The thorium–carbonyl oxygen bond distance, Th–O(4) 2.453 (4) Å, in **1** is comparable to the related distances in several thorium–β-diketonate complexes (**4**), 2.37–2.49 Å, and $Th[CF_3C(O)CHC(O)CH_3]_4 \cdot H_2O$[22] (**6**), 2.39 (1) and 2.46 (2) Å. In the latter two

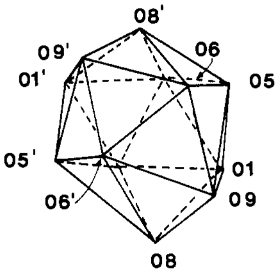

Figure 3. Representation of the oxygen atom coordination polyhedron about the thorium atom.

complexes, each ligand has one short and one long Th–O distance and the long distance compares well with Th–O(4) in **1**. The Th–O(1) and Th–O(4) distances, therefore, suggest that the DEDECMP ligands may not be tightly bonded to the thorium atom.

The Th–O(nitrate) bond distances range from 2.573 (4) to 2.678 (5) Å with an average distance of 2.638 Å. These distances are similar to the related distances in other thorium nitrate complexes containing bidentate nitrate ligands. For example, the complex $MgTh(NO_3)_6 \cdot 8H_2O$[23] has 12 nitrate oxygen atoms surrounding the thorium atom with an average Th–O distance of 2.63 Å. In addition, **3** has a range of Th–O(nitrate) distances of 2.52–2.58 Å[19] and **5** has Th–O(nitrate) distances of 2.61–2.64 Å.[21]

The coordination number for Th(IV) formed by the bidentate nitrate ions and neutral DEDECMP ligands is 12. The

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resulting distorted icosahedral coordination polyhedron is shown in Figure 3. A summary of nonbonded oxygen atom–oxygen atom separations is available in the supplementary data (Table S-3). Several investigators have reported examples of thorium(IV) coordination numbers of 12, and factors responsible for these unexpectedly high coordination numbers have been briefly discussed.[19,21,23] It has been suggested that the packing in those structures containing nitrate ions is stabilized by short O···O nitrate oxygen atom nonbonded interactions, the thorium(IV) cation size, and the empty 5f electronic configuration. Indeed, the structure of **1** shows two nonbonded oxygen–oxygen atom distances O(5)–O(6), 2.148 (6) Å, and O(8)–O(9), 2.147 (7) Å, which are significantly shorter than the sum of oxygen atom ionic radii, 2.8 Å. The short nitrate ion edge distances represent the "bite" distance in these bidentate ligands, and they are similar to distances reported for $MgTh(NO_3)_6 \cdot 8H_2O$[23] and **3**.[19] Lastly, the stability of the coordination number of 12 in **1** is further indicated by a comparison of potential coordination choices. In **3**, the maximum coordination number available to thorium is 10 since the two phosphoryl ligands each offer only one coordination site. In **1**, however, the carbamylmethylenephosphonate ligands offer the ability to serve as monodentate or bidentate ligands producing 10- or 12-coordinate structures. Apparently, the bidentate DEDECMP ligand bonding mode and a 12-coordinate structure are favored.

The structure of the DEDECMP ligands in **1** also is of interest. The ligands clearly exist in the neutral form, and the phosphorus atom environment is characteristic of a tetrahedral phosphate group. The P(1)–O(1) bond distance, 1.478 (4) Å, is slightly longer than the average P═O distance, 1.462 Å, in a variety of tetrahedral phosphate compounds.[24] It has been noted that metal ion coordination to the phosphoryl oxygen atom results in dramatic reduction in P═O stretching frequencies, but few significant changes in P═O bond distances are found upon metal-ion attachment to the oxygen atom.[24] This is consistent with the similarity of P═O bond distances in **1** and $[Hg\{(C_2H_5O)_2P(O)CHC(O)N(C_2H_5)_2\}NO_3]_2$, 1.45 (1) Å,[9] and $Co_3[(C_2H_5O)_2P(O)CHC(O)CH_3]_6$,[25] 1.464 (5) Å. The P═O bond distances in a variety of thorium phosphoryl coordination complexes also are similar as represented by **3**, 1.43 (2) and 1.47 (2) Å, **4**, 1.54 Å, and **5**, 1.33–1.61 Å (average 1.42 Å). The lengths of these bonds compared to the theoretical single-bond P–O distance, 1.71 Å, is usually used as evidence for a degree of π bonding in the unit. The carbonyl distance, C(2)–O(4) 1.256 (6) Å, also is similar to distances observed in several related complexes including $[Hg\{(C_2H_5O)_2P(O)CHC(O)N(C_2H_5)_2\}NO_3]_2$,[9] 1.24 (2) Å, $Co_3[(C_2H_5O)_2P(O)CHC(O)CH_3]_4$,[25] 1.30 (1) Å, **4**,[20] 1.28 Å (average), and **6**, 1.25 Å.[22] The P–O (alkyl) and P(1)–C(1) bond distances also are similar to those distances reported in the dimeric mercury complex.[9] The bond angles about the phosphorus atoms are clearly tetrahedral, and the bond angles about the carbonyl carbon atom are consistent with a trigonal-planar geometry. The P(1)–C(1)–C(2) angle is 110.5 (4)°.

The nitrate groups are planar with a range of N–O bond distances, 1.213 (8)–1.270 (7) Å, which compares well with the ranges found in several thorium nitrate complexes.[19,21,23] The N–O distances associated with the oxygen atoms bonded to the thorium atom, N(2)–O(5) 1.270 (7) Å, N(2)–O(6) 1.265 (8) Å, N(3)–O(8) 1.263 (8) Å, and N(3)–O(9) 1.256 (7) Å, are long compared to the unique N–O bond distances, N(2)–O(7) 1.213 (8) Å and N(3)–O(10) 1.219 (8) Å. In addition, the bite angles, O(5)–N(2)–O(6) 115.9 (5)° and O(8)–N(3)–O(9) 116.9 (5)°, were smaller than the remaining O–N–O angles. This scheme of N–O bond distances and O–N–O bond angles is consistent with the assigned bidentate bonding character of the nitrate ions.

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Supplementary Material Available: Listings of structure factors, thermal parameters, and selected nonbonded distances (29 pages). Ordering information is given on any current masthead page.

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