solvent mixture for development of the plate.

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Registry No. 1 (R = H), 56200-27-2; 1 (R = CH_3), 69140-73-4; **5** (R′ = Ph; X = Br), 70-11-1; **5** (R′ = *p*-BrC_6H_4; X = Br), 99-73-0; **5** (R′ = *p*-$CH_3OC_6H_4$; X = Br), 2632-13-5; **5** (R′ = *p*-C_6H_4; X = Br), 135-73-9; **5** (R′ = $(CH_3)_5C_6$; X = Cl), 57196-63-1; **6** (R′ = Ph), 98-86-2; **6** (R′ = *p*-BrC_6H_4), 99-90-1; **6** (R′ = *p*-($H_3OC_6H_4$), 100-06-1; **6** (R′ = $(CH_3)_5C_6$), 2040-01-9; **6** (R′ = *p*-PhC_6H_4), 92-91-1; **7** (R = H; X = Br), 12079-79-7; **7** (R = CH_3; X = Br), 82182-10-3; **7** (R = H; X = Cl), 12128-23-3; **8**, 12132-04-6; **9**, 82182-11-4; $[(CH_3)_5C_5](H)(CO)BrMo(CHCOC_6H_4Br$-*p*), 82182-12-5; camphor, 76-22-2; α-bromocamphor, 76-29-9.

Synthesis and Structure of a Supersandwich Pentanuclear Uranium(IV) Complex,[1] $U\{Ni[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)\}_4$

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Summary: The combination of $\{Ni[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)^-\}[NH_4^+]$ with UCl_4 in THF results in the formation of an unusual red pentanuclear coordination complex $U\{Ni[P(O)(OCH_3)_2]_2(C_5H_5)\}_4$. Single-crystal X-ray analysis of the complex reveals that the four anionic nickel phosphonate ligands are bonded to a central uranium atom in a bidentate fashion through U—O═P interactions.

Several metalla β-diphosphinites containing the structural unit $M[(-PR_2O-)_2H]$ (R = alkyl, aryl, or alkoxy) have been prepared,[3] and the deprotonated complexes $M[(-PR_2O)_2^-]$ may act as bidentate ligands toward another metal ion in a fashion similar to metalla β-diketonates.[4] For example, Werner and co-workers[5] have prepared several complexes of the general type $M\{Co[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)\}_2$, and a crystal structure analysis for $Co\{Co[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)\}_2$ revealed two anionic ligands, $\{Co[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)^-\}$, bonded in a bidentate fashion to a central Co(II) atom through the phosphoryl oxygen atoms. Subsequently, Kläui[6] has reported the formation of lanthanide complexes, of the general type $Ln\{Co[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)\}_3$. In addition, Werner and Khac[7] have also reported syntheses of $\{Ni[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)^-\}(H^+)$ (**1**) and spirocyclic trinuclear coordination complexes of the anion 1^- with Co(II), Zn(II), and $Ni(NH_3)_2^{2+}$. However, the structures have not been determined, and little is known about the chemistry of these interesting compounds. The coordination properties of phosphito and phosphonato ligands with lanthanide, actinide, and transition-metal ions are of interest in our program,[8] and we report here the formation and crystal structure determination of an unusual pentanuclear "supersandwich" complex of 1^- with uranium(IV).

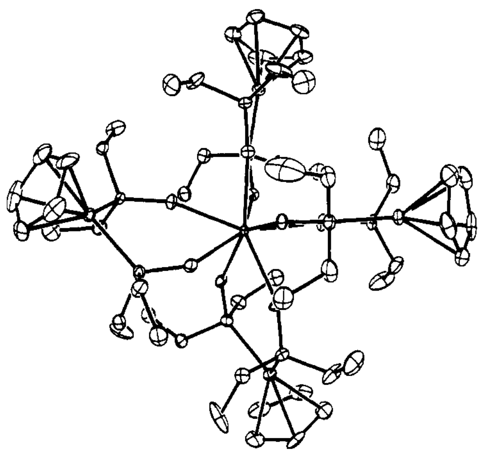

Figure 1. Molecular geometry for $U\{Ni[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)\}_4$ (20% probability ellipsoids).

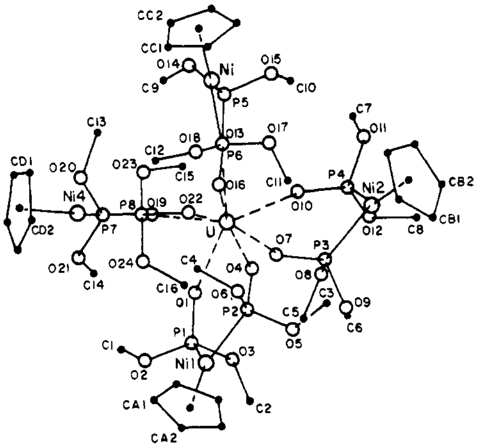

Figure 2. Atom labeling scheme for $U\{Ni[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)\}_4$.

Table I. Average Interatomic Distances (Å) and Angles (Deg) for $U\{Ni[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)\}_4$

	Bond Distances		
U—O	2.355 (10)	P═O	1.51 (1)
Ni—P	2.126 (4)	P—O	1.61 (1)
Ni—C	2.12 (2)	C—O	1.41 (3)
U···Ni	4.750 (2)		
	Bond Angles		
U—O═P	150.1 (6)	Ni—P═O	121.7 (4)
P—Ni—P	96.1 (2)	Ni—P—O	109.6 (5)
X—Ni—P[a]	131.9 (5)	P—O—C	121.1 (12)

[a] X = centroid of Cp ring.

A tetrahydrofuran (THF) solution of UCl_4 (45 mg, 0.12 mmol) was added to a THF slurry of $\{Ni[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)^-\}[NH_4^+]$[7] (195 mg, 0.50 mmol), and the resulting mixture was stirred under nitrogen for 24 h. The cloudy mixture was then filtered under nitrogen to remove NH_4Cl formed in the reaction. The red filtrate was evaporated to dryness, and a red solid, **2**, was collected and characterized by infrared spectroscopy.[9] The red solid

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is stable in dry air for several days.

The accurate stoichiometry and structure of **2** were determined by single-crystal X-ray diffraction analysis.[10] The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. Crystal data are as follows: $a = 15.851$ (4) Å, $b = 15.496$ (4) Å, $c = 23.061$ (3) Å; $\beta = 93.80$ (2)°; $V = 5652.0$ (2) Å^3; $\rho_{calcd} = 1.89$ g cm^{-3}; μ(Mo Kα) = 43.2 cm^{-1}; $F(000) = 3200$; $R_F = 0.065$ and $F_{wF} = 0.067$ for 7116 unique reflections with $F^2 \geq 3\sigma(F^2)$.[12] A view of the molecular structure of **2** is shown in Figure 1, an atom-labeling scheme is shown in Figure 2, and averaged intramolecular bond distances and angles are presented in Table I.[12]

The X-ray analysis clearly reveals that **2** contains a central uranium atom surrounded by four **1**$^-$ ligands, and each ligand is bonded to the uranium atom in a bidentate fashion through the phosphoryl oxygen atoms. The eight phosphoryl oxygen atoms form a square antiprism which closely resembles the coordination polyhedron found for $U(acac)_4$.[13] The U-O(phosphoryl) distances range from 2.346 (9) to 2.381 (10) Å (average 2.355 Å). These distances are similar to the U-O(phosphoryl) distance reported for $UO_2(NO_3)_2(Bu_3PO)_2$, 2.347 (6) Å,[14] and shorter than the U-O(phosphoryl) distance found for $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$, 2.420 (4) Å.[15] The U-O(phosphoryl) distances also are similar to the U-O(carbonyl) distances in $U(acac)_4$, 2.23 (3)-2.37 (4) Å.[13] The long U···Ni separations (average 4.750 (2) Å) indicate that there is no significant interaction between these metal atoms. The accompanying U—O═P angles in the inner coordination sphere range from 148.9 (6) to 152.0 (6)° (average 150.1 (6)°). The individual oxygen atom-oxygen atom "bite" distances range from 2.74 (1) to 2.82 (1) Å (average 2.79 Å), and the remaining O-O edge distances on the polyhedron range from 2.75 (1) to 3.33 (1) Å (average 2.93 Å).

The structural features of the coordinated anion **1**$^-$ also are of interest. The phosphoryl P═O bond distances range from 1.49 (1) to 1.52 (1) Å (average 1.51 (1) Å), and these distances are on the long end of the bond distance range usually associated with metal-coordinated phosphoryl groups.[8,16] The $P-OCH_3$ bond distances range from 1.59 (1) to 1.63 (1) Å (average 1.61 (1) Å),[17] and these distances also are on the long end of P-OR bond distances found in many complexes containing $(RO)_2(X)P{=}O{-}M$ units.[16] The average bond angles in this unit are as expected: Ni—P═O = 121.7 (4)°, Ni—P—O = 109.6 (5)°, and P—O—C = 121.1 (12)°.

The Ni-P bond distances range from 2.116 (4) to 2.139 (4) Å (average 2.126 (4) Å). Few comparative data are available for similar bonding arrangements; however, the distances are comparable to a number of Ni-P distances for classical nickel phosphite coordination compounds.[16] The Ni-C atom bond distances associated with the Ni-Cp interaction average 2.12 (2) Å, and these distances are similar to distances reported for a number of $CpNi(PPh_3)R$ complexes.[18]

Lukehart has previously suggested that the combination of $UCp_2(NEt_2)_2$ and the rhena β-diketone $\{Re(CO)_4[C(O)CH_3]_2\}H$ leads to the formation of a trinuclear complex $Cp_2U\{Re(CO)_4[C(O)CH_3]_2\}_2$ (**3**); however, a full description of this complex has not appeared. The synthesis and structure determination of **2** supports the comparison mentioned above between the metalla β-diketonate and metalla β-diphosphonate ligands and indirectly offers some credence to the proposed composition of the trinuclear complex **3**. In addition, **2** represents the first example of a complex containing a metalla β-diphosphonate ligand bonded to an actinide element, and the first structurally characterized example of a mixed transition metal-actinide coordination complex.[19] Additional studies of the coordination properties of **1**$^-$ with organo actinide and lanthanide fragments are in progress.

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Registry No. 2, 82150-24-1; $\{Ni[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)^-\}[NH_4^+]$, 62126-01-6; UCl_4, 10026-10-5.

Supplementary Material Available: A full description of the data collection and structure solution and tables of observed and calculated structure factors, atomic positional parameters, thermal parameters, and bond angles and distances (30 pages). Ordering information is given on any current masthead page.

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(9) Yield: 85%; IR (mull) 1089, 1040, 1005, 835, 797, 762, 720, 623, 590 cm^{-1}. Satisfactory NMR data were not obtained primarily because of the low solubility of **2** in common organic solvents. Single crystals were obtained by slow evaporation of a THF solution of **2**.

(10) X-ray data were collected with a Syntex P3/F automated four-circle diffractometer (Mo Kα radiation, $\bar{\lambda} = 0.71069$ Å), and the structure was solved with the Syntex XTL system. A full description of the data collection and structure solution is available in the supplementary material.[11]

(11) Supplementary material.

(12) Tables of observed and calculated structure factors, atomic positional parameters, and thermal parameters and a full listing of bond angles and distances are available.[11]

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(17) The P(1)-O(3) bond distance is unusually long, 1.69 Å, and the thermal parameters of O(3) are large. A difference map showed another peak close to O(3), and a disorder of O(3) over two sites was indicated.[11] Only one position was found for the attached C(2) atom, and the P(1)-O(3) bond distance was not included in the average bond distance range listed in the text.

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Alkylation of Transition Metal Alkoxides and Aryl Oxides

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Summary: Treatment of transition metal alkoxides and aryl oxides with lithium alkyls gives rise to varying amounts of substitution depending on the metal, alkyl, alkoxide (or aryl oxide) and solvent.

There are numerous examples in the literature of transition metal alkoxides being used as substrates for the synthesis of alkyl compounds.[1] Alkoxides can offer nu-