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Synthesis and Characterization of a Novel Tetranuclear 5f Compound: A New Synthon for Exploring U(IV) Chemistry

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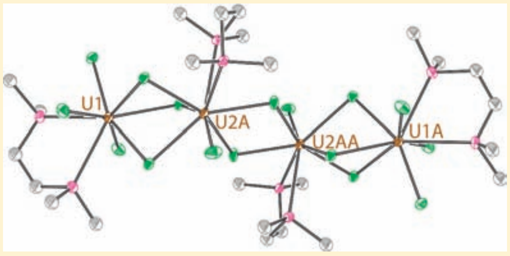
Ⓢ *Supporting Information*

ABSTRACT: In the course of structurally characterizing previously reported complexes based on the 1,2-bis(dimethylphosphino)ethane)) (dmpe) ligand ([$(dmpe)_2UCl_4$] (**1**) and [$(dmpe)_2UMe_4$] (**2**)), we find that adjusting the U/dmpe ratio leads to an unprecedented species. Whereas the use of two or three equivalents of dmpe relative to UCl_4 produces **1** as a blue-green solid, the use of a 1:1 dmpe/UCl_4 stoichiometry yields [$(dmpe)_4U_4Cl_{16}$]·$2CH_2Cl_2$·(**3**·$2CH_2Cl_2$) as a green solid. In turn, **3** is used to prepare a mixed-chelating ligand complex featuring the bidentate ligand 4,4′-dimethyl-2,2′-bipyridine (dmbpy), [(dmpe)(dmbpy)UCl_4] (**4**). The measured magnetic susceptibilities for **1**−**4** trend toward nonmagnetic ground states at low temperatures.



INTRODUCTION

Burgeoning interest in organouranium complexes stems from their potential to impart unusual and/or catalytic reactivity on organic substrates as well as to offer insight into actinide electronic structure.[1−19] The preparation of stable mixed ligand uranium compounds is of importance to realize these goals, as evidenced by recent efforts.[11,13,20−30] Such complexes also aid the understanding of actinide magnetochemistry. The magnetic properties of actinides represent a mixing of properties normally associated with transition metal (magnetic exchange coupling) and lanthanide ions (e.g., spin−orbit coupling).[12] Large spin−orbit coupling may be anticipated to generate anisotropy, relevant to maximizing single-molecule magnet (SMM) blocking temperatures, provided that paramagnetic ground states are achieved. Slow relaxation of magnetization has been observed recently in certain uranium complexes.[12,31,32] A recent effort in our group to control U(IV) paramagnetism and magnetic communication via trigonal bipyramidal coordination of the ion shows some promise in terms of magnetic coupling but is countered by a relatively weak overlap of bridging ligand and metal orbitals attributable to the hardness of the ancillary triamidoamine ligand set.[33]

To improve U−L−M communication, we are pursuing "new" U(IV) building blocks and have become interested in precedent surrounding octacoordinate [$(dmpe)_2UX_4$] (dmpe = 1,2-bis(dimethylphosphino)ethane, X = Cl or Me) complexes. First reported by Andersen et al. in 1981, these species display cubic-like geometries, which in principle allow for paramagnetic f^2 ground states.[34] In addition, the softer dmpe ligands may increase U−ligand orbital overlap and afford greater spin density on acetylide bridging ligands. Finally, fruitful substitution chemistry has been demonstrated, with the chloride ligands replaceable by alkyl and ultimately alkoxide ligands. Similar to our work, and following Scott's precedent,[33,35] these complexes appear suitable for substitution with acetylide-type ligands. From here, elaboration to UM_4 molecular species and/or network solids is envisioned, wherein interesting magnetic properties may be present in the new compounds.

In the process of reproducing Andersen's chemistry for production of [$(dmpe)_2UX_4$] starting materials, we have obtained X-ray-quality crystals of [$(dmpe)_2UCl_4$] (**1**) and [$(dmpe)_2UMe_4$] (**2**), structural data for which have not been reported previously. More significantly, we have found that variation of the U/dmpe stoichiometry leads to a previously unknown tetranuclear complex, [$(dmpe)_4U_4Cl_{16}$]·$2CH_2Cl_2$ (**3**·$2CH_2Cl_2$). This novel tetranuclear complex acts as a "(dmpe)UCl_4" synthon, allowing the preparation of U(IV) complexes with mixed-chelating ligands; synthetic utility is demonstrated via the preparation of [(dmpe)(dmbpy)UCl_4] (**4**) (dmbpy = 4,4′-dimethyl-2,2′-bipyridine). Herein, we describe the preparation, characterization, and structures of the mono- and tetranuclear octacoordinate U(IV) complexes **1**−**4**.

EXPERIMENTAL SECTION

Preparation of Compounds. All manipulations were carried out either inside a dinitrogen-filled glovebox (MBRAUN Labmaster 130) or via standard Schlenk techniques on a dinitrogen manifold. Pentane was distilled over sodium metal, degassed by three freeze−pump−thaw cycles, and stored under an atmosphere of dinitrogen. All other solvents were reagent grade, passed through alumina, degassed, and stored under dinitrogen. The compounds UCl_4,[36] [$(dmpe)_2UCl_4$] (**1**), and [$(dmpe)_2UMe_4$] (**2**) (dmpe = 1,2-bis(dimethylphosphino)ethane) were prepared according to the literature.[34] Methyllithium was titrated prior to use with accurately weighed amounts of menthol

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Table 1. Crystallographic Data[a] for Compounds $[(dmpe)_2UCl_4]$ (1), $[(dmpe)_2UMe_4]$ (2), $[(dmpe)_4U_4Cl_{16}]\cdot 2CH_2Cl_2$ ($3\cdot 2CH_2Cl_2$), and $[(dmpe)(dmbpy)UCl_4]$ (4)

	1	2	$3\cdot 2CH_2Cl_2$	4
formula	$C_{12}H_{32}P_4UCl_4$	$C_{16}H_{44}P_4U$	$C_{26}H_{68}P_8U_4Cl_{20}$	$C_{18}H_{28}N_2P_2UCl_4$
fw	680.09	598.42	2289.69	714.19
color, habit	blue-green cube	yellow block	green rod	light green rod
T, K	120(2)	120(2)	120(2)	120(2)
space group	$P2_12_12_1$	$P4_32_12$	$I4_1/a$	$P2_12_12_1$
Z	12	4	8	4
a, Å	12.6594(5)	12.2692(9)	37.3334(7)	9.2997(2)
b, Å	14.0045(6)	12.2692(9)	37.3334(7)	14.4254(4)
c, Å	41.7425(19)	17.0398(14)	12.9469(3)	18.5866(5)
V, Å^3	7400.5(5)	2565.1(3)	18045.2(6)	2493.43(11)
d_{calcd}, g/cm^3	1.831	1.550	1.686	1.903
GOF	1.02	1.30	1.09	1.03
R_1 $(wR_2)^b$, %	3.09 (5.51)	3.18 (8.41)	5.92 (19.06)	2.43 (4.47)

[a] Obtained with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ for $F_o > 4\sigma(F_o)$.

and 2,2′-bipyridyl. All other reagents were obtained from commercial vendors and used without further purification.

Caution! *Depleted uranium (primary isotope ^{238}U) is a weak α emitter (4.197 MeV) with a half-life of 4.47 × 10^9 years; manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with α- and β-particle counting equipment.*

$[(dmpe)_2UCl_4]$ (1). Liquid dmpe (2.012 g, 13.40 mmol) was added to a stirring slurry of UCl_4 (3.310 g, 8.714 mmol) in 175 mL of dichloromethane, and the resulting green mixture was stirred overnight at ambient temperature. The mixture was filtered, and the volume of the blue-green filtrate was reduced to ca. 5 mL under reduced pressure. Then, the filtrate was maintained at −35 °C for 8 h to afford a blue-green crystalline solid. The solid was collected by filtration and dried in vacuo to yield a blue-green crystalline powder (5.028 g, 85% based on UCl_4). Single crystals suitable for X-ray analysis were grown from a concentrated dichloromethane solution maintained at −35 °C for 8 h. Absorption spectrum (CH_2Cl_2) λ_{max} (ε_M): 458 (61), 509 (44), 529 (43), 591 (36), 632 (16), 654 (19), 668 (47), 686 (208), 699 (173), 852 (8), 920 (18), 934 (19), 960 nm (10 L·mol^{-1}·cm^{-1}). Absorption spectrum ($(CH_3)_2SO$)) λ_{max} (ε_M): 442 (22), 495 (38), 560 (32), 650 (73), 678 (99), 913 nm (17 L·mol^{-1}·cm^{-1}). ^{1}H NMR (293 K, toluene-d_8): δ 2.19 (s, 24 H, PCH_3), −20.56 ppm (s, 8 H, PCH_2); the spectrum matches that reported by Andersen and co-workers,[34] which is not the same as that of free dmpe. ^{1}H NMR (293 K, CD_2Cl_2): δ 2.36 (24 H, PCH_3), −19.4 ppm (8 H, PCH_2). {^{1}H}^{31}P NMR (293 K, CD_2Cl_2): δ −48.01 ppm. The ^{1}H spectrum obtained in CD_2Cl_2 does not match that obtained for free dmpe. The {^{1}H}^{31}P NMR spectrum appears to be dominated by the free dmpe signal (Figure S15, Supporting Information). ^{1}H NMR (293 K, $(CD_3)_2SO$): δ 1.36 (t (j_{12} = 5 Hz) and (j_{23} = 5 Hz), 4 H, PCH_2), 0.96 ppm (s, 12 H, PCH_3). {^{1}H}^{31}P NMR (293 K, $(CD_3)_2SO$): δ −48.69 ppm. Note: the spectra collected in DMSO match those obtained for free dmpe. IR (mineral oil): 631 (w), 646 (w), 705 (m), 722 (m), 771 (w), 815 (w), 830 (w), 867 (m), 934 (m), 994 (w), 1086 (w), 1132 (w), 1156 (w), 1168 (w), 1277 (m), 1291 (m), 1377 (s), 1422 (m), 1461 (s), 2671 (w), 2724 (w), 2840 (s), 2924 (s) cm^{-1}. Magnetic susceptibility (SQUID, 300 K): μ_{eff} = 3.40 μ_B. Anal. Calcd for $C_{12}H_{32}P_4UCl_4$: C, 21.19; H, 4.74. Found: C, 21.27; H, 4.70.

$[(dmpe)_2UMe_4]$ (2). Methyllithium (6.0 mL, 9.8 mmol) was added dropwise to a stirring solution of **1** (1.498 g, 2.203 mmol) in 80 mL of diethyl ether held at −20 °C. The resulting yellow-brown mixture was stirred for 30 min at −20 °C. All volatiles were removed in vacuo to afford a yellow residue. The crude product was extracted into pentane (3 × 10 mL) and filtered, and the volume of the filtrate was reduced to ca. 5 mL under reduced pressure. After standing for 8 h at −35 °C, a yellow crystalline solid formed. The product was collected by filtration and dried in vacuo to yield a dark yellow powder (0.815 g, 62% based on **1**). Single crystals suitable for X-ray analysis were grown from a concentrated pentane solution maintained at −35 °C for 8 h. ^{1}H NMR (213 K, toluene-d_8): δ 11.27 (s, 12 H, UCH_3), −1.53 (s, 24 H, PCH_3), −43.93 ppm (s, 8 H, PCH_2). The spectrum changes significantly upon warming to room temperature; see Figure S16 in the Supporting Information. IR (mineral oil): 629 (w), 641 (w), 695 (m), 723 (m), 770 (w), 826 (w), 862 (m), 889 (w), 939 (m), 966 (w), 997 (w), 1031 (w), 1084 (w), 1134 (w), 1155 (w), 1168 (w), 1278 (m), 1294 (m), 1377 (s), 1422 (m), 1468 (s), 2671 (w), 2725 (w), 2832 (s), 2946 (s) cm^{-1}. Magnetic susceptibility (SQUID, 300 K): μ_{eff} = 3.23 μ_B. Anal. Calcd for $C_{16}H_{44}P_4U$: C, 32.11; H, 7.41. Found: C, 31.34; H, 7.37.

$[(dmpe)_4U_4Cl_{16}]\cdot 2CH_2Cl_2$ ($3\cdot 2CH_2Cl_2$). Liquid dmpe (0.9980 g, 6.647 mmol) was added to a stirring slurry of UCl_4 (2.000 g, 5.265 mmol) in 100 mL of dichloromethane, and the resulting green mixture was stirred overnight at ambient temperature. The mixture was filtered and the green filtrate collected, and the volume was reduced to a volume of ca. 5 mL under reduced pressure. After standing for 8 h at −35 °C, a green crystalline solid formed. The solid was collected by filtration and dried in vacuo to afford a green powder (2.360 g, 85% based on UCl_4). Single crystals suitable for X-ray analysis were grown from a concentrated dichloromethane solution maintained at −35 °C for 8 h. Absorption spectrum ($(CH_3)_2SO$) λ_{max} (ε_M): 442 (11), 469 (8), 496 (21), 560 (17), 650 (41), 678 (57), 906 nm (8 L·mol^{-1}·cm^{-1}). ^{1}H NMR (293 K, CD_2Cl_2): δ 2.35 (48 H, PCH_3), −19.45 ppm (16 H, PCH_2). {^{1}H}^{31}P NMR (293 K, CD_2Cl_2): δ −9.402 (d, j = 56.7 Hz), −12.122 (d, j = 56.7 Hz), −14.834 (d, j = 56.7 Hz), −46.877 ppm (d, j = 54.3 Hz). The ^{1}H spectra obtained in CD_2Cl_2 contain a very small amount of free dmpe (Figure S19, Supporting Information). The {^{1}H}^{31}P NMR spectrum appears to be dominated by the free dmpe signal (Figure S20, Supporting Information). ^{1}H NMR (293 K, $(CD_3)_2SO$): δ 1.35 (br, 4 H, PCH_2), 0.95 ppm (br, 12 H, PCH_3). {^{1}H}^{31}P NMR (293 K, $(CD_3)_2SO$): δ −48.69 ppm. Note: the spectra collected in DMSO match those obtained for free dmpe. IR (mineral oil): 2924 (s), 2840 (s), 2724 (w), 2671 (w), 1462 (s), 1418 (m), 1377 (s), 1296 (m), 1278 (m), 1167 (w), 1155 (w), 1134 (w), 1086 (w), 995 (w), 947 (m), 932 (m), 895 (m), 867 (m), 833 (w), 805 (w), 772 (w), 737 (m), 724 (m), 706 (m) cm^{-1}. Magnetic susceptibility (SQUID, 300 K): μ_{eff} = 5.39 μ_B. Anal. Calcd for $C_{26}H_{68}P_8U_4Cl_{20}$: C, 13.64; H, 2.99. Found: C, 12.83; H, 2.98. Although single crystals have approximately 7.75 CH_2Cl_2 solvate molecules per **3**, elemental analysis of the bulk product best matches the formula $3\cdot 2CH_2Cl_2$. Even so, elemental analysis reveals a deficiency in the observed percent of carbon; however, a small amount of dark gray material remains after combustion, consistent with the production of refractory uranium carbides. Further details are provided in the Supporting Information.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Crystallographically Determined Structures [$(dmpe)_2UCl_4$] (1), [$(dmpe)_2UMe_4$] (2), [(dmpe)(dmbpy)UCl_4] (4), and [$(dmpe)_2U(OPh)_4$]

	1	2	4	[$(dmpe)_2U(OPh)_4$][34]
U−P	2.9939(14)	3.0031(19)	3.0074(20)	3.104(6)
U−N			2.642(6)	
U−C		2.5134(7)		
U−X[a]	2.6480(13)	2.5134(7)	2.6457(18)	2.17(1)
X_{cis}−U−X_{cis}	89.89(5)	94.0(3)	95.33(7)	94.6(4)
X_{cis}−U−X_{trans}	148.54(4)	143.5(4)	151.74(6)	147.2(1)
P−U−P[b]	66.23(4)	66.77(7)	66.02(3)	64.7(6)
N−U−N[b]			62.10(10)	
P_{cis}−U−Y_{trans}[b]	128.95(5)	129.23(5)	135.97(13)	135.5(2.2)

[a] X = Cl, Me, or OPh. [b] dmpe bite angle.

Of the solvents tried (hexanes, pentane, dimethylsulfoxide, dichloromethane, acetonitrile, benzene, toluene, diethyl ether, and tetrahydrofuran), 3 is only readily soluble in dimethylsulfoxide and slightly soluble in dichloromethane.

[(dmpe)(dmbpy)UCl_4] (4). Solid $3{\cdot}2CH_2Cl_2$ (0.292 g, 0.128 mmol) was combined with 4,4′-dimethyl-2,2′-bipyridine (0.095 g, 0.52 mmol) and 15 mL of dichloromethane. The resulting light green mixture was stirred at ambient temperature for 8 h. The mixture was filtered; the filtrate was collected, dried in vacuo, and recrystallized from acetonitrile to afford a light green solid (0.300 g recovered, 82% based on $3{\cdot}2CH_2Cl_2$). Single crystals suitable for X-ray analysis were grown from a concentrated acetonitrile solution maintained at −35 °C for 8 h. Absorption spectrum (CH_3CN) λ_{max} (ε_M): 457 (52), 489 (20), 508 (38), 522 (28), 590 (24), 630 (16), 680 (105), 685 (122), 698 (92), 847 (10), 920 (14), 946 (14), 959 (12), 1075 nm (27 $L{\cdot}mol^{-1}{\cdot}cm^{-1}$). ^1H NMR (293 K, CD_3CN): δ 8.52 (d (j = 5 Hz), 2 H, Ar), 8.26 (s, 2 H, Ar), 7.28 (d (j = 5 Hz), 2 H, Ar), 2.46 (s, 6 H, Ar−CH_3), 2.08 (br, 4 H, PCH_2), 1.38 (br, 12 H, PCH_3). IR (mineral oil): 3735 (w), 2944 (s), 2840 (s), 2724 (w), 2670 (w), 1613 (w), 1596 (w), 1560 (w), 1550 (w), 1460 (s), 1377 (s), 1297 (m), 1278 (m), 1168 (w), 1155 (w), 1134 (w), 1103(w), 1086 (w), 1040 (w), 1009 (w), 991 (w), 947 (m), 932 (m), 894 (w), 867 (m), 820 (w), 770 (w), 722 (m), 670 (w), 647 (w), 633 (w) cm^{-1}. Magnetic susceptibility (SQUID, 300 K): $\mu_{eff} = 2.73\ \mu_B$. Anal. Calcd for $C_{18}H_{28}N_2P_2UCl_4$: C, 30.27; H, 3.95; N, 3.92. Found: C, 30.10; H, 3.80; N, 3.90.

Of the solvents tried (hexanes, pentane, dimethylsulfoxide, dichloromethane, acetonitrile, benzene, toluene, diethyl ether, and tetrahydrofuran), 4 is only readily soluble in acetonitrile.

X-Ray Structure Determinations. Structures were determined for the compounds listed in Table 1. Single crystals were coated with Paratone-N oil in the glovebox and mounted under a cold stream of dinitrogen gas. Single crystal X-ray diffraction data were acquired on a Bruker Kappa APEX II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Initial lattice parameters were obtained from a least-squares analysis of more than 100 reflections; these parameters were later refined against all data. None of the crystals showed significant decay during data collection. Data were integrated and corrected for Lorentz and polarization effects using Bruker APEX2 software, and semiempirical absorption corrections were applied using SCALE with the aid of numerical face indexing.[37] Space group assignments were based on systematic absences, E statistics, and successful refinement of the structures. Structures were solved using the Patterson method and were refined with the aid of successive Fourier difference maps against all data using the SHELXTL 6.14 software package.[38] Thermal parameters for all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens). Selected bond distances and angles for crystals of compounds **1**, **2**, and **4** are collected in Table 2, while those for compound $3{\cdot}2CH_2Cl_2$ are collected in Table 3. All other metric parameters can be found in the CIF files included with the Supporting Information. In the structure of $3{\cdot}2CH_2Cl_2$, there are several disordered components. The dmpe and one of the chloride (Cl2) ligands bound to U1 are disordered over two sites, with a site occupancy ratio refining to 52:48. The dmpe and chloride ligands bound to U2 are also disordered over two sites, with a site occupancy ratio refining to 51:49. For $3{\cdot}2CH_2Cl_2$, thermal parameters for all chemically equivalent disordered atoms were refined anisotropically and restrained to have the same U_{ij} parameters. A dichloromethane solvate molecule (two per U_4 cluster) was found in Fourier difference maps to be disordered over two sites; the site occupancy ratio refined to 54:46. After numerous attempts to model the remaining disorder failed to improve agreement factors, SQUEEZE[39] was used to remove the remaining disordered components. According to the SQUEEZE output, approximately 5.75 dichloromethane solvent molecules are present per U_4 cluster in the void space and were removed. The chemical data presented for $3{\cdot}2CH_2Cl_2$ in Tables 1 and 3 do not include the components removed by SQUEEZE.

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Structure of [$(dmpe)_4U_4Cl_{16}$]$\cdot 2CH_2Cl_2$ ($3{\cdot}2CH_2Cl_2$)

	$3{\cdot}2CH_2Cl_2$
U−P	2.976(8)
U−Cl (bridge)	2.776(5)
U−Cl (terminal)	2.604(6)
U−U	4.0668(7)
Cl_{cis}−$U_{terminal}$−Cl_{cis}	90.95(19)
Cl_{cis}−$U_{terminal}$−Cl_{trans}	146.09(12)
P−$U_{terminal}$−P	66.22(15)
Cl_{cis}−$U_{bridging}$−Cl_{cis}	93.8(3)
Cl_{cis}−$U_{bridging}$−Cl_{trans}	142.48(7)
P−$U_{bridging}$−P	67.4(4)

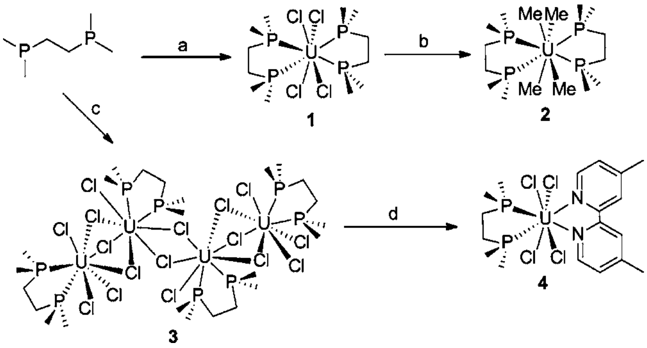
Magnetic Susceptibility Measurements. Magnetic susceptibility measurements were collected using a Quantum Design MPMS XL SQUID magnetometer. Powdered microcrystalline samples were loaded into gelatin capsules in the glovebox, inserted into a straw, and transported to the SQUID magnetometer under dinitrogen. DC magnetic susceptibility data were collected at temperatures ranging from 2 to 300 K at an applied field of 0.1 T. Susceptibility data reproducibility were confirmed by conducting spot checks on samples made in separate batches. Magnetization measurements were collected at temperatures ranging from 2 to 35 K at applied fields of 1, 2, 3, 4, and 5 T. AC magnetic susceptibility data were collected at temperatures ranging from 1.8 to 4 K at an applied AC field of 4 Oe with switching frequencies of 200 and 1488 Hz with and without an applied DC field (see the Supporting Information). Contributions to the magnetization from the gelatin capsule and the straw were measured independently and subtracted from the total measured signal. Data were corrected for diamagnetic contributions using Pascal's constants.[40]

Other Physical Measurements. Electronic absorption spectra were obtained in solution in an air-free glass cell of path length 1 cm on an Agilent 8453 spectrophotometer. ^1H NMR spectra were recorded using a Varian INOVA 500 MHz instrument, and the spectra were referenced internally using residual protio solvent resonances relative to tetramethylsilane (δ = 0 ppm). Infrared spectra were collected on a Thermo Nicolet 380 FTIR spectrometer as mineral oil mulls pressed between sodium chloride plates. Elemental analyses were performed by the Micro-Mass facility at the University of California, Berkeley.

■ RESULTS AND DISCUSSION

Syntheses and Characterizations of [(dmpe)$_2$UX$_4$] (X = Cl, Me). Andersen and co-workers originally reported the synthesis of [(dmpe)$_2$UCl$_4$] (**1**); they also showed that substitution of **1** with methyllithium or phenol affords the tetramethyl (**2**) or tetraphenoxide complexes, respectively.[34] Since complexes **1** and **2** represent potential precursors for uranium acetylide species that may have interesting magnetic properties,[33,35] we have reproduced the syntheses to isolate **1** and **2** for use as building blocks in further studies (Scheme 1).

Scheme 1. Syntheses of Chelating Phosphine Complexes of U(IV): a = 0.5 equiv UCl$_4$ in CH$_2$Cl$_2$ at 23 °C; b = MeLi in Et$_2$O at −20 °C; c = UCl$_4$ in CH$_2$Cl$_2$ at 23 °C; d = dmbpy in CH$_2$Cl$_2$ at 23 °C.



These complexes can be handled under an inert atmosphere in the solid state, although the methyl complex appears to be less thermally stable. For both **1** and **2**, we report infrared spectra and magnetic susceptibilities. Solution colors of the chloride complex **1** in degassed solvents do not change over time, and the compound can be recrystallized from tetrahydrofuran, diethyl ether, and dichloromethane. It is interesting to note that the electronic absorption spectrum of **1** is quite different in dichloromethane compared to dimethyl sulfoxide (Figures S5 and S6, Supporting Information). The dichloromethane solution has a blue-green color, very similar to the solid; however, the color of the dimethyl sulfoxide solution is pale green. From ^{1}H and ^{31}P NMR experiments (Figures S12−S15, Supporting Information), we surmise that the complex maintains structural integrity in the less polar solvent but is labile in the more strongly coordinating dimethyl sulfoxide solvent: free dmpe is observed in DMSO but not in dichloromethane. In contrast, the methyl complex **2** turns black in solution when warmed from −60 °C to ambient temperatures: changes in the ^{1}H NMR spectrum indicate decomposition to as-yet unidentified products (Figure S16, Supporting Information).

As part of the characterization protocol, molecular structures were obtained via single-crystal X-ray analysis (Figure 1). Compound **1** crystallizes in the orthorhombic space group $P2_12_12_1$ (no. 19) with Z = 12. There are three crystallographically independent complex molecules in each unit cell owing to slight variations in the dmpe backbones. The structure of one of the chemically equivalent complexes in **1** is shown in Figure 1, and selected bond lengths and angles are given in Table 2. Single-crystal X-ray analysis of **1** reveals that the uranium ion is ligated by four phosphorus atoms and four chloride ligands. The phosphine ligands are rotated by approximately 90° with respect to each other.

Figure 1. Molecular structures of the U(IV) phosphine complexes in compounds **1** (left) and **2** (right), rendered with 40% ellipsoids. Brown, purple, green, and gray ellipsoids represent U, P, Cl, and C atoms, respectively. Hydrogen atoms are omitted for clarity.

Compound **2** crystallizes in the tetragonal space group $P4_32_12$ (no. 96) with Z = 4; there is one independent complex molecule in each unit cell. The structure of **2** is shown in Figure 1, and selected bond lengths and angles are given in Table 2. Similar to the chloride complex, **2** contains a uranium ion ligated by four phosphorus atoms and four carbon atoms. The phosphine ligands are rotated by approximately 90° with respect to each other.

A New Tetranuclear U(IV) Species as “(dmpe)UX$_4$” Synthon. It has been reported that blue-green **1** can be prepared by the addition of three equivalents of dmpe per UCl$_4$.[34] However, when the reaction is carried out with a deficiency of chelating ligand (1.2:1 dmpe/UCl$_4$), the green tetranuclear species [(dmpe)$_4$U$_4$Cl$_{16}$]·2CH$_2$Cl$_2$ (**3**·2CH$_2$Cl$_2$) is obtained as the only isolable product (Figure 2). Probing the effects of altering reactant stoichiometry via electronic absorption spectroscopy, we find that a 2:1 dmpe/UCl$_4$ ratio exclusively affords the originally targeted mononuclear compound **1**. On larger scales, we find that **1** is isolated from 2:1 dmpe/UCl$_4$ combinations in greater than 75% isolated yield. We note that the electronic absorption spectra of **1** and **3** are virtually identical in DMSO (Figures S6 and S7, Supporting Information); these spectra combined with NMR data indicate that the dmpe ligands dissociate from uranium when **3** is dissolved in DMSO. The electronic absorption spectra are also very similar in CH$_2$Cl$_2$ (Figures S5 and S8, Supporting Information). More importantly, the ^{1}H NMR spectra for **3**

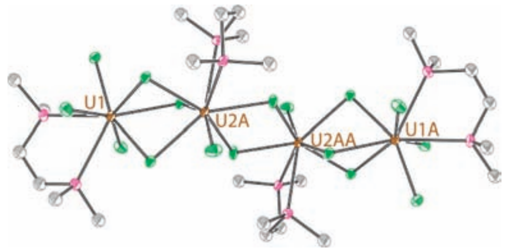


Figure 2. Crystal structure of the U(IV) phosphine complex in **3**·2CH$_2$Cl$_2$, rendered with 40% ellipsoids. Brown, purple, green, and gray ellipsoids represent U, P, Cl, and C atoms, respectively. Hydrogen atoms, solvent molecules, and disordered components in **3**·2CH$_2$Cl$_2$ are omitted for clarity. The complex sits on a crystallographic 2-fold axis.

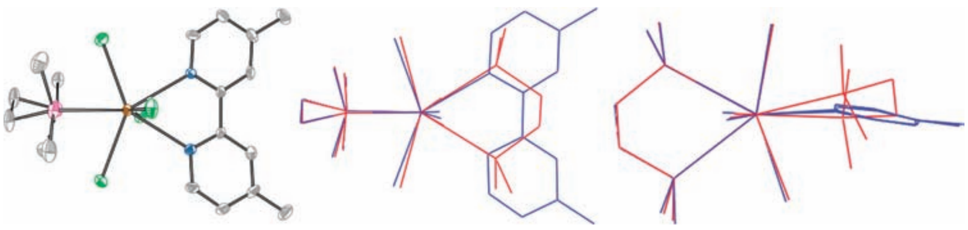


Figure 3. Left: crystal structure of the U(IV) phosphine complex in **4**, rendered with 40% ellipsoids. Brown, purple, green, blue, and gray ellipsoids represent U, P, Cl, N, and C atoms, respectively. Hydrogen atoms are omitted for clarity. Middle and right: overlay of representative U(IV) complexes in compounds **1** (red) and **4** (blue); two different orientations are shown for clarity.

and **1** are also similar, and the main signals are *not* free dmpe (Figures S14 and S19, Supporting Information). The main signal in the $\{^1H\}^{31}P$ NMR spectra for **1** and **3** are consistent with free dmpe; the phosphorus atoms bound to the uranium center may be too broadened to be visible. Interestingly, an additional resonance with complex splitting is observed for **3** in the $\{^1H\}^{31}P$ NMR spectrum (Figure S20, Supporting Information), perhaps indicative of an additional phosphorus environment, as expected for the tetranuclear complex (vide infra) compared to **1**. The spectral data show that **1** and **3** may form similar compounds when dissolved, regardless of solvent; however, the differential solubilities of the mono- and tetranuclear complexes (**3** is much less soluble in dichloromethane than **1**) may give rise to distinct reactivities, as described below.

Compound **3**·2CH$_2$Cl$_2$ crystallizes in the tetragonal space group $I4_1/a$ (no. 88) with Z = 8; there is one independent complex molecule in each unit cell. The structure of **3**·2CH$_2$Cl$_2$ is shown in Figure 2, and selected bond lengths and angles are given in Table 3. Single-crystal X-ray analysis of **3**·2CH$_2$Cl$_2$ reveals that each U(IV) is ligated by two phosphorus atoms and by six chloride ligands. There are two different uranium environments in compound **3**·2CH$_2$Cl$_2$. The terminal uranium atoms have three bridging chloride ligands, while the internal uranium atoms are bridged by five chlorides, three to the external uranium atoms and two to the symmetry equivalent internal uranium. Important average bond distances in **3**·2CH$_2$Cl$_2$ are U−Cl (bridge) = 2.776(5) Å, U−Cl (terminal) = 2.604(6) Å, and U−P = 2.976(8) Å. The U···U separation is 4.0668(7) Å. These values are comparable to other literature reports of uranium complexes featuring bridging and terminal chloride atoms.[41−43]

We have found that **3**·2CH$_2$Cl$_2$ can perform as a "(dmpe)-UCl$_4$" species, allowing for the production of mixed-chelating ligand U(IV) complexes. Combining (green) **3**·2CH$_2$Cl$_2$ with approximately four equivalents of 4,4′-dimethylbipyridine in dichloromethane affords a light green solid. Structural and elemental analyses demonstrate this to be a mixed-chelating ligand U(IV) complex with the formula [(dmpe)(dmbpy)-UCl$_4$] (**4**). The combination of the bis(dmpe) complex **1** with one equivalent of dmbpy in dichloromethane gives an electronic absorption spectrum with similar features to those found in **4**, but molar absorptivities do not match exactly, even if mixtures of **1** and **4** are assumed (Figure S26, Supporting Information). We can conclude that the reactivities of **1** and **3** toward ligand substitution with dmbpy are similar, but mixed-ligand complexes are more cleanly (and economically) isolated by using the tetranuclear complex **3**. We note that NMR studies undertaken in the coordinating solvent acetonitrile show that dmbpy appears to dissociate from **4** but dmpe remains bound (Figure S21, Supporting Information). Going forward, we anticipate that this synthetic control may be expanded and exploited to confer steric and electronic tunability to U−dmpe complexes; exploratory synthetic studies are underway.

Compound **4** crystallizes in the orthorhombic space group $P2_12_12_1$ (no. 19) with Z = 4; there is one crystallographically independent complex molecule in each unit cell. The structure of **4** is shown in Figure 3, and selected bond lengths and angles are given in Table 2. Single-crystal X-ray analysis of **4** shows the uranium ion is bound by two phosphorus atoms, two nitrogen atoms, and four chlorides. The phosphine and bipyridine ligands are rotated by approximately 90° with respect to each other.

Structural Comparisons. Structures were determined via X-ray analysis for the compounds listed in Table 1. The structures of representative uranium complexes are shown in Figures 1−3, and selected bond lengths and angles are given in Tables 2 and 3. For all four structures, the U−Cl and U−P distances are comparable to those of other reported uranium-(IV) phosphine compounds with eight coordinate environments;[12,44−49] the U−P distances are all shorter than those reported for the tetraphenoxide complex [(dmpe)$_2$U(OPh)$_4$].[34] For the structure of **2**, the average U−C distance (2.5134(7) Å) is longer than that reported for other U(IV) compounds, although the structures that contain such U−C bonds are of mainly four-, five-, and six-coordinate uranium centers.[45,50,51]

To compare the U(IV) coordination polyhedra, the SHAPE protocol described by Raymond has been implemented.[52] This program compares all of the dihedral angles in the first coordination sphere of the uranium ion (one for each pair of adjacent triangular planes) to ideal values for selected polyhedra. The shape measure, S, is used to evaluate the degree of distortion from an ideal geometry. S is the minimal variance of dihedral angles along all edges, and the lowest output value represents the most closely related polyhedron.[52] The results of these calculations for compounds **1**−**4** are presented in Table 4. For all U(IV) centers in this study, the local coordination geometries deviate significantly from ideal polyhedra but resemble most closely trigonal dodecahedra (D_{2d}). Interestingly, the U(IV) ions in the bis(dmpe) chloride

Table 4. SHAPE Analyses for Compounds 1−4[a]

	1[b]	**2**	**3**·2CH$_2$Cl$_2$	**4**
$S(D_{2d})$	25.96 (24.77, 25.10, 27.96)	13.36	13.16	14.31
$S(C_{2v})$	26.36 (25.46, 25.25, 28.36)	14.94	14.11	17.07
$S(D_{4d})$	29.49 (28.60, 28.95, 30.92)	17.48	17.19	19.30

[a] The smallest number indicates the most closely related polyhedron shape.[52] [b] Values for **1** are averaged from the three crystallographically independent complexes; numbers in parentheses correspond to individual complexes.

compound **1** are significantly more distorted than in the other complexes. No solvate molecules are present in the structure of **1**, and therefore no obvious hydrogen bonding pathways account for the distortions.

The structures of **1** and **4** were compared to probe distortions caused by the introduction of the 4,4′-dimethylbipyridine ligand into the coordination sphere of the U(IV) ion. The results of this overlay are presented in Figure 3. It can be seen that the chloride ligands in **4** are slightly distorted toward dmpe relative to the orientation in **1**, perhaps due to steric crowding by the larger dmbpy ligand. This is best seen by comparing the Cl−U−Cl and X−U−X (X = P or N) angles (Table 2), where all increase upon replacing dmpe with dmbpy. The effect is strongest for the chlorides in the same plane as dmbpy. Also, a slight curvature of the dmbpy rings is noted, as well as a tilting "down" of the entire dmbpy ligand relative to the plane that bisects the U(dmpe) moiety. Distortions for both **1** and **4** may be due to packing forces; a more detailed investigation of the contributions of weak intermolecular interactions to uranium−ligand binding is in progress.

Magnetic Properties. Due to the nature of crystal field splitting being of approximately the same magnitude as spin−orbit coupling, both of which are greater than kT, the magnetic behaviors of U(IV) compounds are quite complicated.[53−55] Russell−Saunders coupling breaks down and is not sufficiently replaced by a *jj* coupling model.[55] The magnetic moment of the actinides often reflects a mixing, especially at lower temperatures, of the large spin−orbit coupling and ligand field effects into the free ion term. As a result, the term "spin-only" often holds little meaning.[56]

With this in mind, variable temperature magnetic susceptibility data were collected for compounds **1**−**4** and are presented in Figure 4. At 300 K, the measured susceptibilities are 1.45 and 1.31 emu·K·mol^{-1} for compounds **1** and **2**, respectively. These values are somewhat larger than the predicted value of 1.00 emu·K·mol^{-1} for one S = 1 ion with g = 2.00. In contrast, the measured susceptibility for compound **4** at 300 K is 1.13 emu·K·mol^{-1}, which is closer to the predicted value. The $\chi_M T$ values for the mononuclear complexes decrease in a nearly linear fashion to 0.75 (**1**), 0.71 (**2**), and 0.69 (**4**) emu·K·mol^{-1}, respectively, at 90 K. This drop in the measured magnetic susceptibility is most likely due to depopulation of the Stark sublevels. The susceptibilities for compounds **1**, **2**, and **4** all trend toward zero at low temperatures with values of 0.04, 0.03, and 0.02 emu·K·mol^{-1}, respectively, at 2 K. The magnetic behavior of compounds **1**, **2**, and **4** can be interpreted as ground state diamagnetic f^2 species, which are paramagnetic at room temperature due to spin−orbit coupling, temperature-independent paramagnetism (TIP), and thermal population of paramagnetic excited states. This behavior is similar to that observed for other U(IV) compounds in octacoordinate ligand fields,[57−60] with perhaps some contributions from U(IV) single-ion anisotropy.[61,62] Here, it appears that ligand distortions—replacement of Cl with Me or dmpe with dmbpy— make only slight changes to the observed magnetic properties.

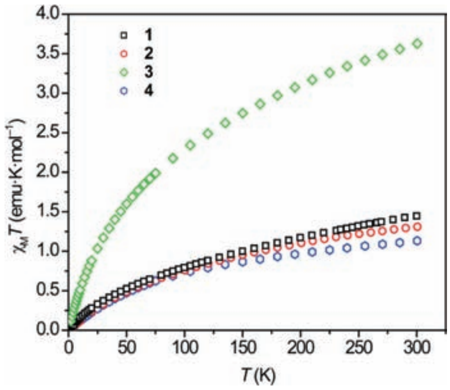


Figure 4. Temperature dependence of the magnetic susceptibility for compounds **1**−**4**, obtained at a measuring field of 1000 Oe. A plot showing the temperature dependence of μ_{eff} values for compounds **1**−**4** appears in the Supporting Information (Figure S30).

Very few examples of magnetic investigations on polynuclear bridging uranium(IV) compounds have been reported.[58,63−65] The room temperature magnetic susceptibility of the tetranuclear compound **3**·2CH$_2$Cl$_2$ (Figure 4) is 3.63 emu·K·mol^{-1}, slightly below the predicted value of 4.00 emu·K·mol^{-1} for four uncoupled S = 1 ions with g = 2.00. The susceptibility decreases gradually to 2.18 emu·K·mol^{-1} at 90 K and is followed by a sharper drop to 0.12 emu·K·mol^{-1} at 2 K. Similar to the mononuclear complexes, the magnetic behavior of compound **3**·2CH$_2$Cl$_2$ can be interpreted as a ground state diamagnetic f^2 species, which is paramagnetic at room temperature, although magnetic coupling *may* be operative, as discussed below.

Comparing **1** and **3**·2CH$_2$Cl$_2$, multiplying $\chi_M T$ values for **1** by 4 gives qualitatively the same temperature-dependent magnetic behavior as **3**·2CH$_2$Cl$_2$, although at 300 K this value is larger than that of the tetranuclear compound (4.51 versus 3.63 emu·K·mol^{-1}).[66] This difference may be due to reduction in complex symmetry and/or covalency in U-ligand bonding, which could remove orbital degeneracy.[55,61,62,67] Although the magnetism in both compounds is dominated by single-ion effects, we cannot entirely rule out the possibility of magnetic exchange between U(IV) ions in **3**·2CH$_2$Cl$_2$ based on susceptibility data alone. The variable temperature magnetic properties for UCl$_4$ have been interpreted as showing Curie−Weiss behavior (θ = −28.8 K and C = 1.726) and having a nonmagnetic ground state and a low-lying paramagnetic first excited state (at 110 cm^{-1}).[68] The negative Weiss constant is consistent with antiferromagnetic coupling of paramagnetic centers, but spin−orbit coupling could account for most of the downturn in the susceptibility-temperature product. Ephritikhine and co-workers reported the synthesis and magnetic characterization of the dinuclear U(IV) complex [L^{1}U$_2$(μ-Cl)$_2$Cl$_2$] (H$_4$L^1 = [*N*,*N*:*N*′,*N*′-bis(2,2′-dihydroxy-3,3′-dimethylidene-5,5′-di-*tert*-butylbiphenyl)benzene-1,2-diamine]);[58] the $\chi_M T$ value of 3.00 emu·K·mol^{-1} at 300 K is larger than expected for two free 5f^2 ions, but its decrease with the temperature to a value of 0 emu·K·mol^{-1} at 2 K is argued to include a contribution from antiferromagnetic coupling. The decrease in $\chi_M T$ in that compound is more rapid than observed with our tetranuclear complex **3**.

The magnetization plots of compounds **1** and **3**·2CH$_2$Cl$_2$ (Figure S27, Supporting Information) both exhibit nonsuperposition of isofield data, a hallmark of magnetic anisotropy. The data for **3**·2CH$_2$Cl$_2$ plotted on a per uranium basis match very closely to the data for mononuclear **1**. We provisionally take this as evidence *against* antiferromagnetic exchange coupling occurring between U(IV) ions in **3**. At the minimum, it would appear that single ion effects obscure any exchange interactions in the tetranuclear complex.

To ascertain if the tetranuclear $\mathbf{3}\cdot 2CH_2Cl_2$ displays characteristics of a single-molecule magnet, AC susceptibility measurements were obtained with and without a perpendicularly applied 0.1 T DC field. No frequency dependence of the AC susceptibility was observed (Figure S28, Supporting Information).

■ SUMMARY AND OUTLOOK

In the course of structurally characterizing complexes **1** and **2** for uranium magnetochemical studies, we have isolated the tetranuclear compound $[(dmpe)_4U_4Cl_{16}]\cdot 2CH_2Cl_2$ ($\mathbf{3}\cdot 2CH_2Cl_2$) and find that it acts as a "(dmpe)UCl_4" synthon for the preparation of mixed chelating-ligand U(IV) complexes, as evidenced by the synthesis of $[(dmpe)(dmbpy)UCl_4]$ (**4**). All of the compounds presented here display magnetism indicative of nonmagnetic ground states, consistent with those described elsewhere in the literature.[51,54,64,67,69−78] If there is magnetic coupling between U(IV) ions in the tetranuclear complex **3**, it is obscured by U(IV) single-ion behavior. Nevertheless, the capability to make heteroleptic complexes offers opportunities for exploring steric and electronic tuning of the uranium ion, with implications for utilizing actinide elements in the generation of new SMMs, and for further probing actinide−ligand bonding.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic and full magnetic property characterizations (pdf) as well as X-ray crystallographic files (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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