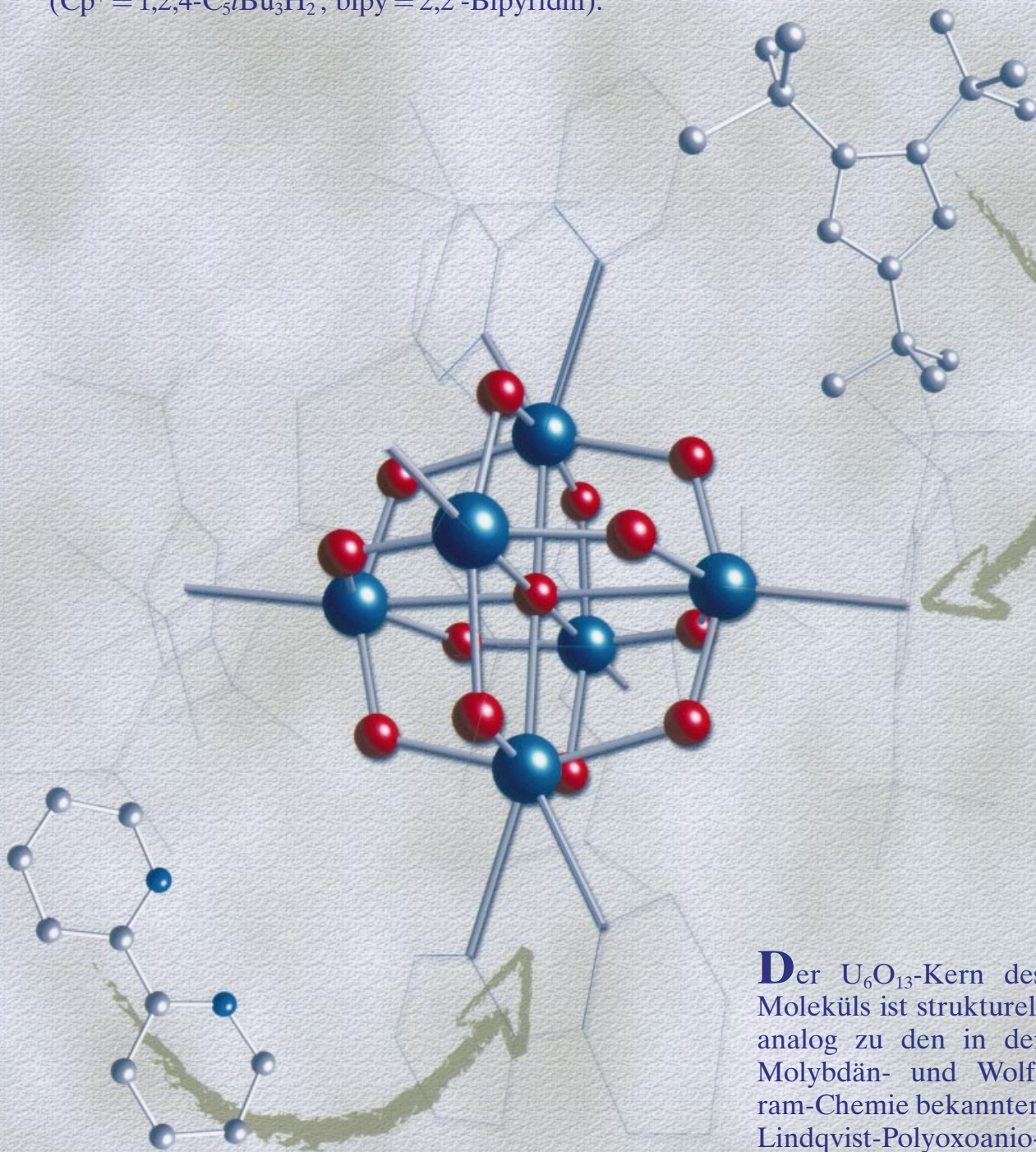


Die Oxidation von Uran-Vorstufenkomplexen mit sperrigen peripheren Cyclopentadienylliganden führt zu dem Cluster $[\text{Cp}^{\ddagger}_4\text{U}_6\text{O}_{13}(\text{bipy})_2]$ ($\text{Cp}^{\ddagger} = 1,2,4\text{-C}_5\text{tBu}_3\text{H}_2$; bipy = 2,2'-Bipyridin).

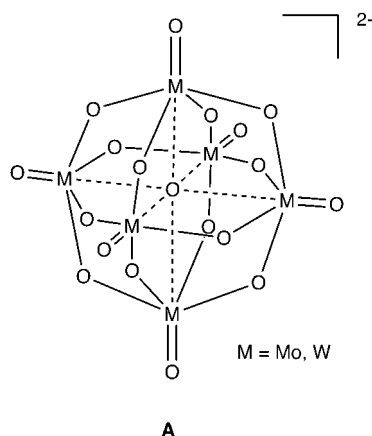


Der U_6O_{13} -Kern des Moleküls ist strukturell analog zu den in der Molybdän- und Wolfram-Chemie bekannten Lindqvist-Polyoxoanionen und liefert ein lange Zeit fehlendes Bindeglied zwischen der Strukturchemie des Urans und seiner Geschwister aus der 6. Nebengruppe. Weitere Informationen hierzu finden sich auf den folgenden Seiten.

Synthesis and Structural Characterization of the First Uranium Cluster Containing an Isopolyoxometalate Core**

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Polyoxometalate ions of the general formula $[M_xO_y]^{z-}$ ($M = \text{Mo}, \text{W}$; less commonly $\text{V}, \text{Nb}, \text{Ta}$) form a large and diverse class of inorganic clusters that are of broad interest due to the unique bonding and structures associated with the cluster framework, the electrochemical and magnetic properties of the reduced heteropoly blue ions, and because of the resemblance of these species to metal oxide surfaces utilized in heterogeneous catalysis.^[1–3] Applications of these clusters have been directed at oxidation catalysts, medical sensors, and solid-state devices. Although cluster topologies may vary, each member within this class exhibits uniform structural features in which MO_6 octahedra are linked by shared vertices or edges ($\mu_2\text{-O}$), but not by faces ($\mu_3\text{-O}$).^[4] One of the prototypes is the octahedral $[\text{M}_6\text{O}_{19}]^{2-}$ unit (**A**), or Lindqvist structure, which contains an $[\text{M}_6\text{O}_{13}]$ cluster core with each metal also coordinated by a terminal oxo ligand.



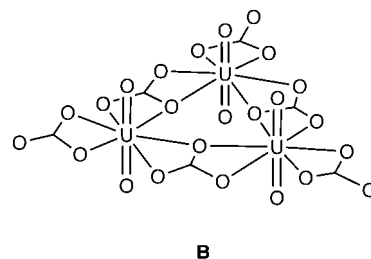
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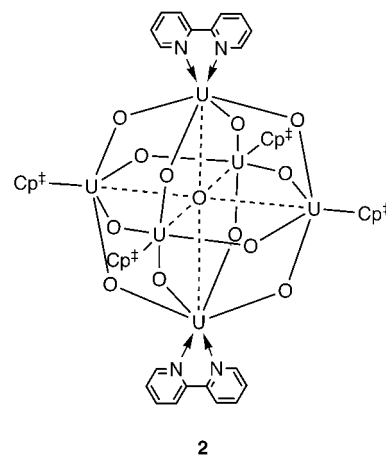
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Although a varied assortment of isopolyoxometalate clusters have been synthesized since the 19th century, all examples have been restricted to the Group 5 and 6 metals listed above, with Mo and W comprising the vast majority of derivatives. For potential extension of this chemistry to other elements, uranium may initially seem a logical candidate based on comparable chemical properties to Mo and W , and has been incorporated into heteropolyanions as either U^{IV} ions^[5] or uranyl (UO_2^{2+}) ions,^[6] but the structural requirements for cluster formation preclude a traditional *aqueous* synthesis of a homoleptic isopolyoxouranate species. Uranium(vi) does in fact share with Mo^{VI} and W^{VI} the strong $\text{M}=\text{O}$ π bonding necessary to terminate a structure, but as shown in **B**^[7] the



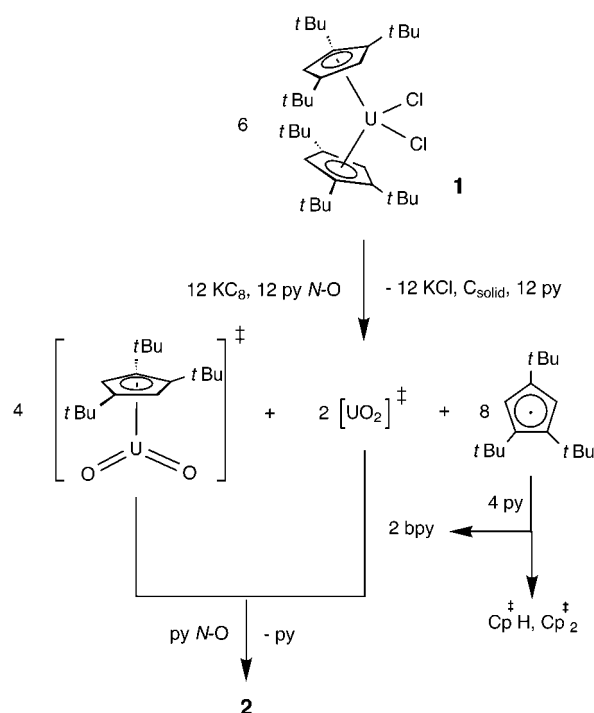
dominance of the *trans*-dioxouranyl unit in aqueous media still permits oligomerization along the equatorial plane, whereas discrete cluster topologies (as in **A**) require stable *cis*-dioxo geometries met by d^0 metals such as Mo^{VI} and W^{VI} .

We report herein how the above problems have been obviated under nonaqueous conditions, such that the genre of isopolyoxometalate derivatives is now extended to include an unprecedented uranium structural analogue **2**, which contains a core unit similar to that in **A**. Although obtained serendipitously in an attempted synthesis of an organometallic



dioxouranium(vi) complex, the results delineate some unique attributes of the actinides, as well as the combination of fortuitous circumstances, that led to the isolation and stabilization of this uranium cluster. The structural and electronic properties of **2** are assessed in the context of the exhaustive studies conducted previously on transition metal polyoxometalates.

We have previously reported an efficient synthesis of bis(imido)uranium(vi) complexes of the general formula $[(C_5Me_5)_2U(=NR)_2]$ by the direct reduction of two azide molecules RN_3 at the uranium center.^[8] This method could not be extended, however, to the preparation of analogous bis(oxo) derivatives $[(C_5Me_5)_2U(=O)_2]$ by using pyridine *N*-oxide; all attempts thus far have generated decomposition products, one of which is the pentamethylcyclopentadienyl dimer $(C_5Me_5)_2$. Considering that steric protection might inhibit potential decomposition pathways, we employed similar reaction conditions using the bulkier cyclopentadienyl derivative $[Cp^*UCl_2]$ (**1**; $Cp^* = 1,2,4-tBu_3C_5H_2$) as the uranium(vi) starting complex. Reduction of **1** with two equivalents of KC_8 in THF, followed by an addition of two equivalents of pyridine *N*-oxide (Scheme 1), was conducted in



Scheme 1. Intermediate species and by-products in the proposed mechanism for the formation of **2**.

an attempt to produce the organometallic dioxo species $[Cp_2^*UO_2]$ (**3**). However, the cluster compound $[Cp_4^*(bpy)_2][U_6O_{13}]$ (**2**) was isolated instead as the main product (54% yield) from this reaction. The complex was not readily characterized in solution (no 1H NMR is observed).

Single crystals of **2** suitable for X-ray diffraction were obtained by slow evaporation of a solution of **2** in toluene.^[9] The X-ray crystal structure for **2** (Figure 1) reveals six uranium atoms arranged in approximate octahedral symmetry, with an interstitial μ_6 -oxo group O(7) situated in the center of the cluster. Tetragonal compression of the uranium octahedron is observed along the U(1)-O(7)-U(1A) axis. Twelve other oxo ligands form μ_2 -O bridging interactions to uranium centers around the cluster framework to furnish the $[U_6O_{13}]$ core that mimics the isopolyoxometalate Lindqvist structure. In the Lindqvist structure, however, a terminal oxo ligand on each metal center would normally complete the

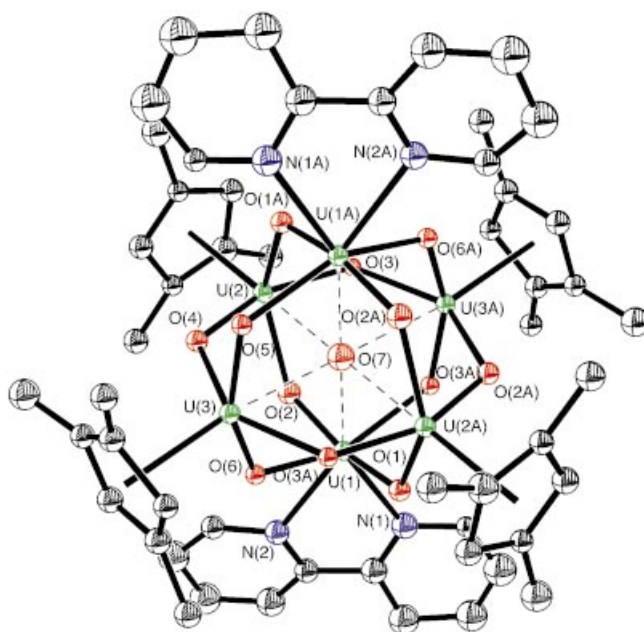
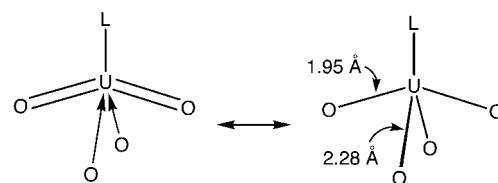


Figure 1. Molecular structure of **2** (methyl carbon atoms of *tert*-butyl groups are omitted for clarity). Bond lengths [$\text{\AA}$]: U(1)-O(1) 1.924(14), U(1)-O(2) 1.905(14), U(1)-O(5) 2.301(11), U(1)-O(6) 2.231(12), U(1)-O(7) 2.4865(8), U(2)-O(7) 2.6353(8), U(3)-O(7) 2.6671(7).

coordination sphere, whereas in **2** these terminal sites are occupied instead by either an η^5 - Cp^* ligand (on the “equatorial” uranium atoms U(2), U(2A), U(3) and U(3A)), or by a chelating bipyridine (bpy) ligand (on the “axial” uranium atoms U(1) and U(1A)). The presence of terminal ligands other than oxo groups has been noted in isopolyoxometalates ions,^[10] but with the notable exception of organoimido functionalities,^[11] only one terminal oxo ligand is typically substituted. In this example, all six are missing. Furthermore, in the transition metal analogues all of the bridging interactions are approximately equivalent, as reflected in similar $M-O_{\text{bridging}}$ bond lengths throughout the M_6 cluster. In marked contrast, in the U_6 cluster there is a distinct pattern between short and long $U-O_{\text{bridging}}$ distances, such that the LUO_4 ($L = Cp^*$ or bpy) coordination sphere at each uranium center features an approximately *trans* O-U-O unit that is elongated, and another *trans* O-U-O unit that is shortened. As illustrated in the resonance structure in Scheme 2, this bond length alternation is suggestive of the *trans*-dioxouranyl unit that pervades aqueous uranium coordination chemistry. However, a modest bending of the $O=U=O$ angles in **2** (between 20° and 30° away from the near linear geometry found in most uranyl complexes) arises from angular bridging interactions to the other uranium centers that encompass the cluster.



Scheme 2. Resonance structures for the LUO_4 ($L = Cp^*$, bpy) units in **2**.

In classical isopolyoxometalate cluster compounds the metals are invariably in their maximum oxidation state, save for $[\text{V}_{18}\text{O}_{42}]^{12-}$, in which each vanadium atom is a $d^1 \text{V}^{\text{IV}}$ system.^[12] In comparison, 13 oxo ligands and four Cp^+ ligands add up to an overall charge of 30^- in neutral **2**, which distributed over six uranium centers gives an average oxidation state of U^{V} (f^1) for each metal. This assessment is supported by the magnetic susceptibility measurements obtained for **2**; a plot of $1/\chi_{\text{M}}$ versus T is shown in Figure 2.

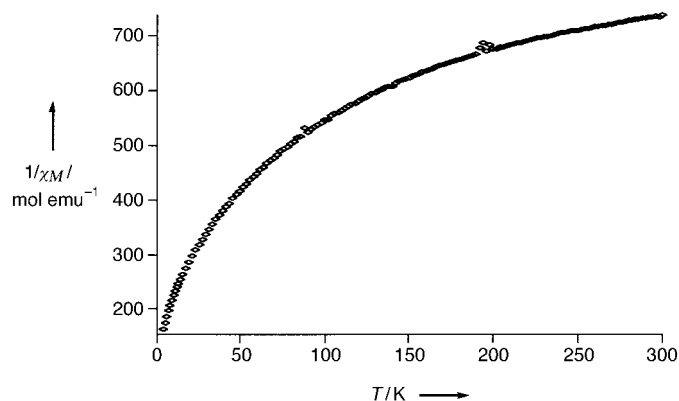


Figure 2. Magnetic susceptibility plot of $1/\chi_{\text{M}}$ versus T (χ_{M} = molar magnetic susceptibility, T = temperature) between 5–300 K.

The curve is consistent with six U^{V} centers behaving as independent paramagnets, although very weak antiferromagnetic exchange (anticipated for highly asymmetric U–O–U bridges) may be suggested by the low magnetic moment ($\mu_{\text{eff}} = 1.8 \mu_{\text{B}}$ per uranium center at 300 K). In contrast, analogous $d^1 \text{V}^{\text{IV}}$ polyoxometalates show much stronger antiferromagnetic coupling across the oxo bridges.^[13]

An important feature of transition metal polyoxometalates is that many derivatives undergo multielectron reduction. The fully oxidized Lindqvist structures are rather limited in this regard, however, as only two electrons can be reversibly added to these species. This behavior differs significantly from that of the uranium cluster **2**, which already possesses reduced U^{V} centers (based on the magnetic susceptibility data), yet is evidently capable of assimilating still more electrons. The cyclic voltammetric behavior (see Supporting Information) shows two distinct regions of irreversible electroactivity. One region at -2.0 V versus the ferrocenium/ferrocene couple is likely attributable to the direct reduction of U^{V} centers, while the second region at -3.0 V is probably associated with electron addition into the coordinated bipyridine rings. Irreversible oxidation is observed at $+1.5 \text{ V}$, suggesting the loss of electrons from the U^{V} centers. Consistent with the observation that oxidation is irreversible, attempts to chemically oxidize the species have so far only resulted in degradation of the cluster.

Regarding the origin of the components that make up **2**, it is plausible that the intended product $[\text{Cp}_2^+ \text{UO}_2] \text{ (3)}$ is initially formed as a reactive intermediate that decomposes by reductive homolytic $\text{Cp}^+ \text{--U}$ cleavage to give $[\text{Cp}^+ \text{UO}_2]$ and a Cp^+ radical (Scheme 1). $[\text{Cp}^+ \text{UO}_2]$ is the fragment that occupies the four equatorial uranium sites, while the other two

sites are occupied by UO_2 units resulting from the loss of a second Cp^+ radical. The fate of the Cp^+ radicals that are generated include: 1) coupling with another Cp^+ radical to give Cp_2^+ , or 2) abstraction of an α -hydrogen from pyridine (released during the reaction with pyridine N -oxide) to generate $\text{Cp}^+ \text{H}$. Both of these organic by-products are observed in the ^1H NMR spectrum of the reaction mixture. The coupling of two pyridyl radicals accounts for the otherwise puzzling formation of bipyridine, which importantly acts as a trapping ligand for the axial UO_2 units. That a similar result (or any tractable product) is not observed in the corresponding synthetic attempt to form $[(\text{C}_5\text{Me}_5)_2\text{UO}_2]$ may derive either from the increased stability of the Cp^+ radical versus a (C_5Me_5) radical, or from greater kinetic stability conferred on **2** by the sterically bulky Cp^+ ligands.

Finally, we address the circumstances that may have provided for the stabilization of this uranium polyoxometalate derivative, where such an example was seemingly unattainable before. As mentioned earlier, the main obstacle within aqueous media has been the incompatibility of the *trans*-uranyl species with the *cis*-dioxo geometry necessary for cluster formation. However, this problem has apparently been eliminated simply by the fortuitous replacement of the terminal oxo groups in **A** with organic functionalities in **2**. In addition to providing steric protection, this substitution removes the *cis*-dioxo geometry that is so unfavorable for uranium; hence, based on the unique asymmetric oxo bridges present in **2**, this cluster actually comprises six *trans*-dioxo (“uranyl-like”) moieties. The extensive bridging interactions that connect these uranyl building blocks are promoted by nucleophilic oxo groups attached to the electron-rich uranium(v) centers. This behavior is reminiscent of cation–cation complexes in neptunyl(v) NpO_2^+ chemistry^[14, 15] (isolable uranyl(v) species are currently unknown), and similar nucleophilic interactions from uranyl(vi) oxo ligands have been noted in rare examples where strong donor equatorial ligands are employed.^[16] Thus, ironically, the incorporation of **2** as a structural analogue into a family of complexes traditionally associated with transition metals derives primarily from one of the attributes (uranyl ion complexation) that most distinguishes actinide chemistry.

Experimental Section

$[[1,2,4-(\text{Me}_3\text{C})_3\text{C}_3\text{H}_2]_2\text{Mg}]$: Dibutylmagnesium (88 mL, 1 M in heptane) was added to 1,2,4-(Me_3C) $_3\text{C}_3\text{H}_2$ (41.25 g, 0.175 mol).^[17] The heptane was removed under reduced pressure, and the pale yellow solution was heated to 130°C for three days. Upon cooling to room temperature, the mixture solidified. The solid was redissolved in pentane (200 mL) and filtered. The volume of the filtrate was reduced until solid began to precipitate. The mixture was warmed to redissolve the solid, then cooled to -20°C . Two crops of white crystals were collected by filtration. Recrystallization of the second crop was necessary to remove residual 1,2,4-(Me_3C) $_3\text{C}_3\text{H}_2$. Yield: 28.45 g (66 %). ^1H NMR (C_6D_6 , 30°C): $\delta = 6.1$ (4H), 1.5 (36H), 1.4 (18H); elemental analysis (%) calcd for $\text{C}_{34}\text{H}_{58}\text{Mg}$: C 83.2, H 11.9; found: C 82.9, H 12.0; EI MS: m/z : 490 [M^+]; the parent ion isotopic cluster was simulated: (calcd. %, obsd. %): 490 (100, 100), 491 (52, 52), 492 (26, 26), 493 (7, 7).

1: $[[1,2,4-(\text{Me}_3\text{C})_3\text{C}_3\text{H}_2]_2\text{Mg}]$ (12.1 g, 0.025 mol) and UCl_4 (8.9 g, 0.023 mol) were suspended in toluene (250 mL) in a 500-mL Schlenk flask under an argon atmosphere. Freshly dried pyridine (50 mL) was added to the suspension, and the mixture was stirred at reflux for one day. The solution was cooled to room temperature and the solvent removed under reduced

pressure. The red solid residue was extracted with hexane (300 mL) and filtered. The volume of the filtrate was reduced to 100 mL and cooled to -20°C . Two crops of dark red crystals were collected by filtration. Yield: 11.6 g (65%). M.p. $192-194^{\circ}\text{C}$; ^1H NMR (C_6D_6 , 30°C): $\delta = 29.7$ (4H, $\nu_{1/2} = 110$ Hz), 9.5 (36H, $\nu_{1/2} = 12$ Hz), -19.4 (18H, $\nu_{1/2} = 7$ Hz); elemental analysis (%) calcd for $\text{C}_{34}\text{H}_{58}\text{Cl}_2\text{U}$: C 52.7, H 7.48; found: C 52.6, H 7.55; EI MS: m/z : 774 [M^+]; the parent ion isotopic cluster was simulated: (calcd. %, obsvd. %): 774 (100, 100), 775 (38, 39), 776 (71, 71), 777 (25, 25), 778 (14, 14), 779 (5, 4).

2: THF (30 mL) was added to a mixture of KC_8 (140 mg, 1.04 mmol) and **1** (400 mg, 0.52 mmol). A dark green color was generated immediately in the solution upon the addition of solvent. The mixture was stirred for 2 h, after which a solution of pyridine *N*-oxide (100 mg, 1.05 mmol) in THF (25 mL) was added. The dark green color of the solution immediately turned dark reddish brown. The reaction mixture was stirred for 12 h, after which the solvent was removed under vacuum and the residue extracted with toluene and filtered through Celite. Dark reddish brown crystals of **2** were obtained from a cold (-30°C) concentrated toluene solution. Yield: 275 mg (54%); IR (Nujol): $\tilde{\nu} = 690, 710\text{ cm}^{-1}$ (U–O); elemental analysis (%) calcd for $\text{C}_{109}\text{H}_{156}\text{N}_4\text{O}_{13}\text{U}_6$: C 41.45, H 4.98, N 1.77; found: C 41.91, H 5.40, N 1.53.

The magnetization of crystalline powdered samples of **2** was recorded between 5–300 K at 0.1 T with a SQUID magnetometer (Quantum Design). Values of the magnetic susceptibility were corrected for the underlying diamagnetic increment ($\chi_{\text{dia}} = -1660 \times 10^{-6}\text{ cm}^3\text{ mol}^{-1}$) by using tabulated Pascal constants and the effect of the blank sample holder (gelatine capsule/quartz wool).

Cyclic voltammetric studies were conducted by using a Perkin–Elmer Princeton Applied Research Corporation (PARC) Model 263 potentiostat under computer control using M270 software. Samples were run in 0.1 M tetrabutylammonium hexafluorophosphate solution in tetrahydrofuran at a platinum working electrode with a silver wire quasi-reference electrode in either a PARC microcell in the glove box or in a Schlenk cell. Measured potentials were calibrated by using the ferrocene/ferrocenium couple ($E_{1/2} \sim 0.55\text{ V}$ vs. NHE).

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 [9] Crystallographic details for **2**: a dark red crystal ($0.12 \times 0.08 \times 0.04\text{ mm}$) was mounted from Paratone N oil onto a glass fiber and immediately placed on a Bruker P4/CCD/PC diffractometer. A hemisphere of data was collected by using a combination of ϕ and ω scans, with 30 second frame exposures and 0.3° frame widths. A total of 14413 reflections ($-14 \leq h \leq 15$, $-20 \leq k \leq 20$, $0 \leq l \leq 28$) were collected at $T = 203(2)\text{ K}$ in the θ range of $1.49-23.32^{\circ}$ of which 14413 were unique ($R_{\text{int}} = 0.0000$); $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The structure was solved by using direct methods and difference Fourier techniques (SMART Version 4.210, Bruker Analytical X-ray Systems, Inc., 1996). All non-hydrogen anisotropic temperature factors were restrained by using the ISOR option, and hydrogen atoms were placed in calculated ($d_{\text{C-H}} = 0.96\text{ \AA}$ for methyl, $0.93\text{ \AA}$ for methyl) positions. The residual peak and hole electron density was 1.770 and $-1.791\text{ e \AA}^{-3}$. The absorption coefficient was 7.641 mm^{-1} . The least-squares refinement converged normally with residuals of $R1 = 0.0686$ ($I > 2\sigma(I)$), $wR2 = 0.1610$, and $\text{GOF} = 1.152$ (F^2); $\text{C}_{109}\text{H}_{156}\text{N}_4\text{O}_{13}\text{U}_6$, space group $P\bar{1}$ (no. 2), triclinic $a = 13.8298(7)$, $b = 18.681(1)$, $c = 25.335(2)\text{ \AA}$, $\alpha = 80.118(1)^{\circ}$, $\beta = 76.867(1)^{\circ}$, $\gamma = 72.803(1)^{\circ}$, $V = 6050.9(6)\text{ \AA}^3$, $Z = 2$, $F(000) = 2916$, $\rho_{\text{calcd}} = 1.733\text{ g cm}^{-3}$. Crystallo-

graphic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-160613. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Rational Molecular Design and EPC Synthesis of a Type VI β -Turn Inducing Peptide Mimetic**

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Besides the specific role of proline for the structure of proteins, experimental and simulation studies indicate that proline-containing sequence motives can act as molecular hinges, swivels, and switches and, thus, are involved in biological signaling processes.^[1] Furthermore, *cis/trans*-prolyl isomerization that can be catalyzed by rotamase enzymes is critical for the folding process.^[2] Recently, pseudoproline inducing a *cis*-peptide bond were introduced into the V3 loop of GP120 of HIV-1, which suggests that a *trans/cis* isomerization resulting in formation of a type VI β -turn conformation plays a crucial role in the infection process.^[3] Thus, the creation of type VI β -turn model systems is of interest for the discovery of molecular probes to gain detailed insight into the intermolecular interaction processes. Using appropriate con-

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