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Crystal Structures of $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$ and $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(p\text{-}tolyl)]_2$; Compounds with Asymmetrically Bridging Primary Amide and Imide Groups

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Crystal Structures of $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$ and $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(p\text{-}tolyl)]_2$; Compounds with Asymmetrically Bridging Primary Amide and Imide Groups

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Abstract

The trivalent uranium amide, $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$, was prepared by the acid-base reaction between $[(Me_3Si)_2N]_3U$ and mesitylamine. The pKa's of $(Me_3Si)_2NH$ and mesitylamine are not particularly helpful in predicting the outcome of the proton transfer reaction; this is probaby due to the change in pKa upon coordination to the uranium center. X-Ray crystallographic analysis (-75°C) of the compound; monoclinic $P2_{1/n}$, a = 16.997(1)Å, b = 11.854(1)Å, c = 15.121(2)Å, β = 99.10(1)°, V = 3008Å^3, Z = 2; shows that the mesitylamide (the amide hydrogen atom was located but not refined) asymmetrically bridges the two $[(Me_3Si)_2N]_2U$ centers with U-N distances of 2.453(3)Å and 2.646(3)Å and a U-N-U angle of 102.9(1)°. The tetravalent uranium organoimide, $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(p\text{-tolyl})]_2$ was prepared in the reaction of $[(Me_3Si)_2N]_3UCl$ and LiN(H)(p-tolyl), a reaction which is thought to involve a proton transfer step. X-ray crystallographic analysis (-118°C) of the compound; triclinic, $P\bar{1}$, a = 9.792(1)Å, b = 12.212(1)Å, c = 14.580(3)Å, α = 62.00(1)°, β = 65.86(1)°, γ = 80.80(1)°, V = 1403Å^3, Z = 1; shows that the p-tolylimide asymmetrically bridges the two $[(Me_3Si)_2N]_2U$ centers with U-N distances of 2.378(3)Å and 2.172(2)Å and a U-N-U angle of 105.8(1)°. The asymmetry is ascribed to electronic (hybridization) effects. Magnetic susceptibility studies from 5-280K on both compounds show no magnetic interaction between the U···U centers.

Reactions of metal amides with protic acids (eq. 1) are of general synthetic utility.[1] The reaction in eq. 1 is exothermic when the pKa of the amine is higher than that of HER.

$$MNR_2 + HER \rightarrow MER + HNR_2 \qquad (1)$$

The concept of acidity is very useful in organic chemistry but the extension to inorganic or organometallic chemistry is not without problems since the most extensive tabulations are in solvents such as water[2a] or dimethylsulfoxide[2b] and these solvents have limited utility in organometallic and inorganic synthesis. It has been shown recently, however, that pKa values determined in dimethylsulfoxide or cyclohexylamine for charge delocalized ion pairs are very close to those values determined in tetrahydrofuran;[2cd] this is an encouraging result as it suggests that extension of acidity concepts to inorganic and organometallic synthesis could be a useful concept in designing a synthetic strategy utilizing pKa's of protic acids. Unfortunately, tables of pKa values often do not contain the precise compound of interest though extrapolation usually gives a satisfactory estimate. Perhaps the most difficult aspect of applying acidity concepts to metal systems is the effect of coordination on acidity; generally coordination of a Lewis base increases its acidity since the metal center can stabilize the negative charge on the conjugate base.[3]

We have recently shown that metallocenes of cerium will react with alcohols and thiols whose pKa's (in water) are less than 16, the pKa of C_5H_6 in water.[4] Proton transfer reactions of tetravalent uranium amides were first studied in the 1940's, though published in 1956, by Gilman.[5a] Uranium alkoxides can be prepared by reaction of alcohols (pKa's in water range from 15 to 20) and uranium thiolates can be prepared by reaction of thiols (pKa's in water are ca. 10) with $U(NEt_2)_4$. The pKa of Et_2NH is much larger than that of the alcohols and thiols, though the exact value is unavailable; the pKa of $(Me_2CH)_2NH$ in tetrahydrofuran is 36 and it is reasonable to assume that the pKa of Et_2NH is similar.[6a] Several proton transfer reactions of uranium dialkylamides have been described.[5]

The pKa of $(Me_3Si)_2NH$ in tetrahydrofuran has been estimated to be either 30[6a] or 26;[6b] it is expected that $U[N(SiMe_3)_2]_3$ would react with phenols as described by

Sattelberger *et al.*[5h] In addition, trivalent lanthanide silylamides, $M[N(SiMe_3)_2]_3$, undergo proton transfer reactions with protic acids whose pKa's are less than that of $(Me_3Si)_2NH$.[7] Since the pKa of primary arylamines is ca. 30, pKa (H_2O) of $PhNH_2$ = 28[2a] and pKa(Me_2SO) is 31,[2b] it is by no means obvious whether aniline will react with $U[N(SiMe_3)_2]_3$ by proton transfer or if the Lewis base will just form a coordination complex with the uranium silylamide. In this paper we show that $U[N(SiMe_3)_2]_3$ has a rather extensive proton transfer chemistry.

Synthesis and Structure

Addition of aniline, p-methylaniline, or ammonia to $U[N(SiMe_3)_2]_3$[8] gives tan, insoluble solids from which no pure compounds could be obtained. Mesitylamine also gives an insoluble, blue precipitate that is insoluble in hexane and toluene, though soluble in tetrahydrofuran in which it decomposes. Even though the blue precipitate cannot be characterized in solution, dark blue plates can be obtained by layering a pentane solution of the amine on a pentane solution of $U[N(SiMe_3)_2]_3$. The blue crystals that were obtained were shown to be $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$ by X-ray crystallography, Figure I. The compound can be viewed as resulting from the proton transfer reaction shown in eq. 2, even though the pKa of mesitylamine should be greater than that of $(Me_3Si)_2NH$; the

$$2[(Me_3Si)_2N]_3U + 2H_2NAr \rightarrow [(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(Ar)]_2 + 2(Me_3Si)_2NH \quad (2)$$

pKa of mesitylamine is not known, but it should be one or two units higher than aniline.[2a] The assumption that the reaction proceeds by coordination followed by proton transfer suggests that the pKa of mesitylamine decreases upon coordination.

The ORTEP diagram of $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$ is shown in Figure I, Table I lists the positional parameters and Table VI lists the crystal data. The dimer has idealized C_{2h} symmetry with the inversion center located at the center of the U_2N_2 rhombus so that the mesityl groups are anti relative to the U_2N_2 plane. The two $U[N(SiMe_3)_2]_2$ centers are asymmetrically bridged by the two mesitylamide ligands with U-N(3) and U-

N(3') distances of 2.453(3)Å and 2.646(3)Å, respectively, and U-N(3)-U' and N(3)-U-N(3') angles of 102.9(1)° and 77.2(1)°, respectively. The hydrogen atom on the mesitylamide group was located in the difference Fourier map, but would not refine, so it was placed on N(3) with a distance of 0.87Å. The U-N-C (mesityl) angles are also asymmetric, the U-N(3')-C(1') angle is 94.3(2)° and the U-N(3)-C(1) angle is 135.8(2)°. The asymmetry in U-N (mesityl) distances and U-N-C (mesityl) angles result in some close U···C (mesityl) contact distances, U···C(1'), U···C(6'), and U···C(6'a) are 3.10, 3.32, and 3.39Å, respectively. It is difficult to rationalize these distortions other than to note that the size of the two groups (mesityl and hydrogen) on the bridging ligand are very different, resulting in a highly anisotropic steric requirement. The solid state structure is a manifestation of these anisotropic forces, the result of which is the shortest possible bond distances which minimize ligand-ligand repulsions.

The identity of the bridging group as mesityl amide, N(H)(mesityl), rather than mesitylimide, N(mesityl), rests largely on the X-ray structural result that, unfortunately, is not unequivocal since, though the hydrogen atom on N(3) is found in the difference Fourier map, it could not be refined. Ignoring the placed hydrogen atom, the geometry at N(3) is non-planar, consistent with a bridging amide rather than a bridging imide group since in two other uranium compounds with bridging imides, $(MeC_5H_4)_4U_2(\mu\text{-}NSiMe_3)_2$ and $(MeC_5H_4)_4U_2(\mu\text{-}NPh)_2$,[9] the geometry is planar. No infrared spectroscopic evidence was found for an N-H stretching frequency, perhaps due to its low intensity or because it is hidden under other ligand absorptions in the 3200-3000 cm^{-1} region. The insolubility precludes other solution spectroscopic characterization. Two ways to differentiate between the U(III)-N(H)(mesityl) and U(IV)-N(mesityl) formulation are magnetic susceptibility studies (see later), and X-ray crystallographic examination of an authentic specimen of $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(mesityl)]_2$.

We have been unable to remove the proton and oxidize the uranium center from $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$ directly and an alternative strategy was devised. The

uranium (IV) silylamide, $[(Me_3Si)_2N]_3UCl$, reacts with a number of nucleophiles giving $[(Me_3Si)_2N]_3UR$.[10] If R were the amide of a primary amine, then, perhaps, a proton transfer reaction would generate the bridging organoimide as shown in eqs. 3-5 or 6-8.

$$[(Me_3Si)_2N]_3UCL + LiN(H)(R) \rightarrow [(Me_3Si)_2N]_3UN(H)(R) + LiCl \quad (3)$$

$$[(Me_3Si)_2N]_3UN(H)(R) \rightarrow [(Me_3Si)_2N]_2UNR + (Me_3Si)_2NH \quad (4)$$

$$[(Me_3Si)_2N]_2UNR \rightarrow \frac{1}{2}\ [(Me_3Si)_2N]_4U_2(\mu\text{-}NR)_2 \quad (5)$$

$$[(Me_3Si)_2N]_3UCl + 2LiN(H)(R) \rightarrow [(Me_3Si)_2N]_2U(NHR)_2 + LiCl + LiN(SiMe_3)_2 \quad (6)$$

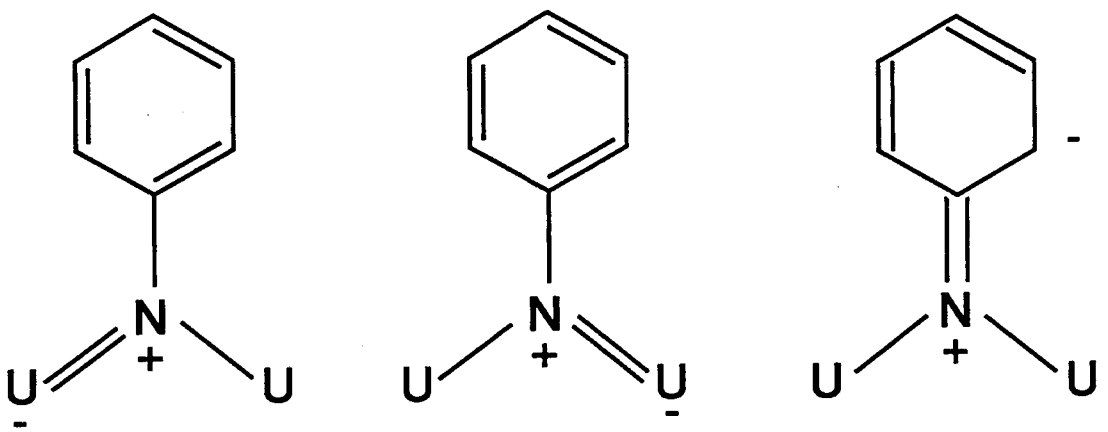
$$[(Me_3Si)_2N]_2U(NHR)_2 \rightarrow [(Me_3Si)_2N]_2UNR + NH_2R \quad (7)$$

$$[(Me_3Si)_2N]_2UNR \rightarrow \frac{1}{2}\ [(Me_3Si)_2N]_4U_2(\mu\text{-}NR)_2 \quad (8)$$

These two possibilities may be distinguished since they differ in the outcome of the reactions shown in eq. 3 and eq. 6. Addition of a suspension of LiN(H)(p-tolyl) in hexane to $[(Me_3Si)_2N]_3$ UCl gives the bridging p-tolylimide; we have been unable to isolate pure materials by using LiN(H)(mesityl). Crystallization of the brown-red solid from hexane gives $[(Me_3Si)_2N]_4\ U_2\ [\mu\text{-N-(p-tolyl)}]_2$ in 65% yield, Figure II. The physical properties are provided in The Experimental Section. The amide, $[(Me_3Si)_2N]_3\ U[N(H)(p\text{-tolyl})]$ was obtained by an alternative synthetic route[9b] and it does not eliminate $(Me_3Si)_2$ NH on pyrolysis. These two observations strongly support the sequence of reactions symbolized by eqs. 6-8 as the most reasonable set of elementary reactions leading to the net reaction.

The ORTEP diagram of the organoimido dimer is shown in Figure II, positional parameters are shown in Table II, and crystal data are shown in Table VI. The molecule has idealized D_{2h} symmetry with the inversion located in the center of the U_2N_2 rhombus. The U-N (tolyl) distances are unequal, U-N(3) is 2.172(3)Å and U-N(3') is 2.278(3)Å, respectively, as are the U-N-C (tolyl) angles; the U-N(3)-C(1) and U'-N(3)-C(1) angles are 138.2(2)° and 113.9(2)°, respectively. The geometry at the bridging nitrogen is planar. The angles within the U_2N_2 rhombus are close to those found in the bridging mesitylamide described above; U-N(3)-U' and N(3)-U-N(3') are 105.8(1)° and 74.2(1)°, respectively.

The asymmetry observed in $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(p\text{-tolyl})]_2$ is similar to that observed in the metallocene derivatives $(MeC_5H_4)_4U_2(\mu\text{-}NR)_2$, where R is Ph or $SiMe_3$; some comparisons are shown in Table III. For the three structures, the averaged U-N distances and U-N-C (aryl), U-N-C ($SiMe_3$), or U-N-U angles are nearly identical suggesting that the effect of the $(MeC_5H_4)_2U$ and $[(Me_3Si)_2N]_2U$ fragments are nearly identical. This similarity in bond property suggests that the extent of the distortion of an individual distance or angle can be rationalized on the basis of the identity of the organic group bonded to the bridging nitrogen atom. The asymmetry in the metallocene examples was ascribed to contributions of three resonance structures A, B, and C, with the azabenzylic resonance structure, C, being largely responsible for the asymmetry in the



A B C

phenylimide structure. The asymmetry in the bridging p-tolylimide group described in this paper is not as great as that found in the bridging phenylimide though greater than that found in the bridging silylimide. This can be rationalized by noting that a methyl group in the para-position of a phenyl ring will make resonance structure C less important than in the phenyl derivative and the asymmetry should be less severe, as observed. This explanation could be tested by structurally characterizing $[(Me_3Si)_2N]_4U_2(\mu\text{-}NPh)_2$, however, we have been unable to isolate this molecule. The explanation given above assumes that the

distortions are of electronic origin and that steric effects and crystal packing forces do not play the dominant role. The structures of the bridging mesitylamide and bridging p-tolylimide offer another illustrative structural comparison, as shown in Table IV. These two compounds have identical terminal ligands and the bridging atoms are also identical though the oxidation state of the uranium atoms differ by one unit. The U(III)-N$(SiMe_3)_2$ distance is 0.06Å longer than the equivalent distance in the U(IV)-N$(SiMe_3)_2$ fragment and the N-U-N angles differ by only 2°, the angle at U(III) being smaller. This small change is as expected since Shannon suggests U(III) in six coordination is 0.04Å larger than U(IV) in six coordination.[11a] The averaged bridging N-U distances are very different in the two molecules, reflecting the multiple bonding and/or the dinegative charge on the nitrogen center in the U(IV) compound. The averaged bridging U-N(imide) distance of ca. 2.23Å in the three structures listed in Table III is ca. 0.2 to 0.4Å shorter than the averaged, bridging U-N(amide) distance in $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]$, Table IV, as expected since the radius of a sp^2-hybridized nitrogen atom is ca. 0.3Å smaller than that of a sp^3-hybridized nitrogen atom.[11b,c] The comparison in bond lengths shown in Table IV supports the contention that $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]$ is a bridging amide rather than a bridging imide.

Magnetic Moments

Magnetic moments of uranium compounds are difficult to understand at the microscopic level since uranium compounds are examples of the intermediate splitting case in which the crystal field splittings are of the same order of magnitude as the spin-orbit coupling which are greater than kT.[12] This is in contrast to the first row transition metal compounds in which the crystal field splitting is much larger than the spin-orbit coupling and kT; in the actinides, the term spin-only has no meaning. Even at the macroscopic level the magnetic moments are difficult to use since the large spin-orbit coupling and the crystal field terms mix into the free ion term and the magnetic moments are a reflection of the

extent of mixing. The values of the magnetic moments for trivalent or tetravalent uranium compounds vary greatly; since the values of μ overlap they are of limited use in determining the oxidation state. The shape of the plot of the inverse of the magnetic susceptibility as a function of temperature is often helpful in deducing oxidation state since at low temperature the ground state of U(IV) compounds is usually an orbital singlet and χ_M^{-1} becomes temperature independent. An isolated f^3 ion cannot be an orbital singlet since the spin is always half-integral. These concepts are illustrated by the plots of χ_M^{-1} as a function of temperature for the dimers described in this paper which are shown in Figure III. The values of the magnetic moments for the U(III) and U(IV) compounds in Table V are similar though the shape of the curves are different, but their meaning is ambigious. The curve for the U(III) compound is temperature dependent and the shape is not unusual.[12c] The curve for the U(IV) is different from what is usually observed, viz., at low temperature the curve becomes independent of temperature.[12] This behavior presumably is due to the small energy difference between the ground state singlet and the first excited state. At this time the reason for the deviation from normal U(IV) paramagnetism is unknown. In addition, no magnetic coupling between the spins on the uranium atoms is apparent to 5K and the molecules behave as isolated paramagnets.

Experimental Section

All experimental studies were done as previously described using the instruments described earlier.[8]

$[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$. A solution of 2,4,6-trimethylaniline (0.09 mL, d = 1.0 g/mL, 0.67 mmol) in 20 mL of pentane was carefully layered on top of a solution of $U[N(SiMe_3)_2]_3$[8] (0.50 g, 0.70 mmol) in 30 mL of pentane. The two solutions were allowed to stand undisturbed for 24 h. The mixture was then carefully filtered, and the dark blue-green crystals were isolated (0.12 g, 25%), m.p. 191-195°C. A small

amount of brown solid was always present on the sides of the glassware after the two solutions had mixed. The product was not soluble in aliphatic or aromatic hydrocarbon solvents and attempts at recrystallization from tetrahydrofuran led to deposition of a brown, oily substance. The ^{1}H NMR spectrum could not be obtained due to insolubility of the compound. Anal. Calcd. for $C_{42}H_{94}N_6Si_8U_2$: C, 36.5; H, 6.85; N, 6.07. Found: C, 35.6; H, 6.95; N, 5.69. IR: 1300 w, 1292 w, 1250 m, 1242 m, 1215 w, 1207 w, 1154 w, 964 s, 931 w, 872 m, 855 s, 845 s, 817 m, 771 m, 755 w, 737 w, 731 w, 720 w, 654 m, 606 m cm^{-1}.

$[(Me_3Si)_2N]_4U_2[\mu\text{-}N(p\text{-tolyl})]_2$. To a solution of p-toluidine (0.10 g , 0.93 mmol) in 30 mL of hexane was added 0.24 mL of n-BuLi (3.98 M in hexane, 0.96 mmol). A white precipitate formed immediately. This mixture was added to a suspension of $ClU[N(SiMe_3)_2]_3$[10a] (0.70 g, 0.93 mmol) in 20 mL of hexane. The color changed from pinkish-orange to bright gold and then slowly darkened to red-brown. The mixture was stirred six hours, filtered and the volume of the filtrate was reduced to 4 mL. Slow cooling to -15°C yielded red bricks (0.40 g, 65% yield), m.p. 230-233°C. ^{1}H NMR (C_6D_6, 20°C): 12.66 (2H), 6.20 (2H), 1.21 (3H), -12.40 (36H). Anal. Calcd. for $C_{38}H_{86}N_6Si_8U_2$: C, 34.4; H, 6.53; N, 6.33. Found: C, 33.1; H, 6.34; N, 5.96. IR: 1603 w, 1491 m, 1250 s, 1216 s, 1174 m, 955 s, 931 s, 844 s, 816 s, 772 m, 756 m, 727 m, 677 w, 657 m, 607 m, 525 m, 480 m, 385 m cm^{-1}.

X-Ray Crystallographic Studies. $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$. Deep blue crystals of the compound were obtained by slow diffusion of a pentane solution of 2,4,6-trimethylaniline with a pentane solution of $U[N(SiMe_3)_2]_3$. The crystal, sealed inside of a quartz capillary, used for data collection was of approximate dimensions 0.39 mm x 0.34 mm x 0.16 mm. It was transferred to an Enraf-Nonius CAD-4 diffractometer and cooled to -75°C by a cold flow apparatus previously calibrated by a thermocouple

placed at the sample position. The crystal was centered in the beam. Accurate cell dimensions and orientation matrix were determined by a least-squares fit to the setting angles of the unresolved MoKα components of 24 symmetry related reflections with 2θ between 24 and 30°. The search yielded the same unit cell as the precession photographs and confirmed the Laue symmetry, $P2_{1/n}$.

The 4351 raw intensity data were converted to structure factor amplitudes and their esds by correction for scan speed, background and Lorentz-polarization effects. Inspection of the intensity standards showed no appreciable decay in intensity (1.7%) during data collection. Inspection of the azimuthal scan data showed a variation $I_{min}/I_{max} = 0.48$ for the average curve. An analytical absorption correction using the measured size and indexed faces of the crystal and a 12 x 14 x 12 gaussian grid of internal points was performed after the solution of the structure had confirmed the stoichiometry of the molecule. The maximum and minimum transmission factors were 0.244 and 0.497, respectively. Removal of redundant and systematically absent data left 3932 unique data.

The structure was solved by Patterson methods and refined <u>via</u> standard least-squares and Fourier techniques. In a difference Fourier map calculated following refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks corresponding to the expected positions of all of the hydrogen atoms were found. All hydrogens, except the unique amido-hydrogen, were included in the structure factor calculations in their expected positions based on idealized bonding geometry. All hydrogens were assigned isotropic thermal parameters 1.3Å^2 larger than the equivalent B_{iso} of the atom to which they were bonded. None of the hydrogens were refined in least squares. The amido-hydrogen was placed in its observed position and the N-H bond length was adjusted to 0.87Å. Attempts to refine the amido-hydrogen with an isotropic thermal parameter were unsuccessful.

$[(Me_3Si)_2N]_4U_2[\mu\text{-}N(p\text{-tolyl})]_2$. Red crystals of the compound were obtained by slow cooling of a saturated hexane solution from room temperature to -25°C. The crystal, inside a quartz capillary, used for data collection was of approximate dimensions 0.45 mm x 0.32 mm x 0.21 mm. It was transferred to an Enraf-Nonius CAD-4 diffractometer and cooled to -118°C. The search yielded the same unit cell as the precession photographs and confirmed the Laue symmetry, $P\bar{1}$.

The 3896 raw intensity data were converted to structure factor amplitudes and their esds by correction for scan speed, background and Lorentz-polarization effects. Inspection of the intensity standards showed no appreciable decay in intensity (< 1.0%) during data collection. Inspection of the azimuthal scan data showed a variation $I_{min}/I_{max} = 0.62$ for the average curve. An empirical correction for absorption, based on the azimuthal scan data, was applied to the intensities. Removal of redundant data left 3696 unique data.

The structure was solved by Patterson methods and refined <u>via</u> standard least-squares and Fourier techniques. In a difference Fourier map calculated following refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks corresponding to the expected positions of all of the hydrogen atoms were found. All hydrogens were included in the structure factor calculations in their expected positions based on idealized bonding geometry. All hydrogens were assigned isotropic thermal parameters 1.3Å^2 larger than the equivalent B_{iso} of the atom to which they were bonded. None of the hydrogens were refined in least squares. All calculations were performed on a DEC Microvax II using locally modified Nonius-SDP[3] software operating under Micro-VMS operating system.

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Supplementary Material. Tables of positional parameters for all of the atoms, Tables of all of the bond lengths and angles, anisotropic thermal parameters, RMS amplitudes of thermal vibrations, and Structure Factor Tables (69 pages). This material is available from the authors.

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Table I. Positional Parameters for the Non-Hydrogen Atoms in $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$. A complete listing of all positional parameters is available as Supplementary Material.

Atom	x	y	z	B(A2)
U	0.48407(1)	0.04242(1)	0.12356(1)	1.805(3)
Si11	0.44996(8)	0.3505(1)	0.14990(9)	2.82(3)
Si12	0.36915(7)	0.1781(1)	0.24657(8)	2.66(3)
Si21	0.53378(8)	-0.1661(1)	0.28583(8)	2.99(3)
Si22	0.64536(7)	0.0318(1)	0.30054(8)	2.48(3)
N1	0.4317(2)	0.2117(3)	0.1713(2)	2.10(7)
N2	0.5614(2)	-0.0378(3)	0.2482(2)	2.15(7)
N3	0.5793(2)	0.0732(3)	0.0198(2)	2.15(7)
C1	0.6589(2)	0.0384(3)	0.0149(3)	2.11(9)
C2A	0.7044(3)	0.2402(4)	-0.0083(3)	3.0(1)
C2	0.7181(2)	0.1146(4)	-0.0039(3)	2.40(9)
C3	0.7927(3)	0.0728(4)	-0.0131(3)	3.3(1)
C4	0.8122(3)	-0.0395(4)	-0.0056(4)	3.7(1)
C4A	0.8938(3)	-0.0823(6)	-0.0178(5)	6.3(2)
C5	0.7548(3)	-0.1127(4)	0.0150(3)	3.2(1)
C6	0.6787(2)	-0.0772(4)	0.0266(3)	2.30(9)
C6A	0.6241(3)	-0.1608(4)	0.0609(3)	2.7(1)
C111	0.3613(3)	0.4274(5)	0.0881(4)	4.8(1)
C112	0.4855(4)	0.4335(4)	0.2540(4)	5.4(2)
C113	0.5291(3)	0.3645(4)	0.0777(3)	3.6(1)
C121	0.2746(3)	0.2609(5)	0.2344(4)	5.2(1)
C122	0.3381(3)	0.0278(4)	0.2300(3)	3.8(1)
C123	0.4190(3)	0.1883(5)	0.3660(3)	4.2(1)
C211	0.4853(4)	-0.1552(5)	0.3884(4)	5.6(1)
C212	0.6167(3)	-0.2694(4)	0.3093(4)	5.3(1)
C213	0.4595(3)	-0.2312(4)	0.1952(3)	3.1(1)
C221	0.6509(3)	0.0400(5)	0.4243(3)	4.4(1)
C222	0.6445(3)	0.1779(4)	0.2559(4)	4.0(1)
C223	0.7404(3)	-0.0323(4)	0.2788(4)	4.1(1)

Table II. Positional Parameters for the Non-Hydrogen Atoms in $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(p\text{-tolyl})]_2$. A complete listing of all positional parameters is available as Supplementary Material.

Atom	x	y	z	B(A2)
U	0.02301(1)	0.11303(1)	0.36131(1)	1.748(3)
Si11	0.0396(1)	0.41941(9)	0.23089(8)	2.60(3)
Si12	0.2824(1)	0.33521(9)	0.31899(8)	2.41(2)
Si21	-0.1013(1)	0.03200(9)	0.21860(7)	2.38(2)
Si22	0.2326(1)	0.0973(1)	0.10515(8)	3.67(3)
N1	0.1354(3)	0.2995(2)	0.2986(2)	2.00(7)
N2	0.0586(3)	0.0823(3)	0.2110(2)	2.15(7)
N3	0.1260(3)	-0.0491(3)	0.4536(2)	2.07(7)
C1	0.2311(4)	-0.1368(3)	0.4322(3)	1.86(8)
C2	0.3725(4)	-0.1413(3)	0.4342(3)	2.47(9)
C3	0.4745(4)	-0.2269(3)	0.4109(3)	2.54(9)
C4	0.4421(4)	-0.3101(3)	0.3836(3)	2.5(1)
C5	0.3012(5)	-0.3074(4)	0.3830(4)	4.4(1)
C6	0.1972(4)	-0.2236(3)	0.4080(3)	3.5(1)
C7	0.5578(5)	-0.3991(3)	0.3541(3)	3.6(1)
C111	-0.1415(4)	0.3538(4)	0.2562(3)	3.3(1)
C112	0.1415(6)	0.4976(5)	0.0764(4)	5.6(2)
C113	-0.0163(5)	0.5394(4)	0.2838(4)	4.7(1)
C121	0.2108(5)	0.3568(4)	0.4492(3)	3.5(1)
C122	0.3950(5)	0.4782(4)	0.1976(4)	4.3(1)
C123	0.4200(4)	0.2093(4)	0.3353(3)	3.2(1)
C211	-0.0891(5)	-0.1199(4)	0.2150(3)	4.2(1)
C212	-0.2472(4)	0.0122(3)	0.3591(3)	2.68(9)
C213	-0.1724(5)	0.1455(4)	0.1093(3)	3.8(1)
C221	0.3742(5)	0.1417(4)	0.1377(3)	4.3(1)
C222	0.2892(6)	-0.0527(5)	0.0948(5)	8.5(2)
C223	0.2404(7)	0.2174(7)	-0.0348(4)	8.2(2)

The Thermal parameter is defined as: $\frac{4}{3}[a^2\beta(1,1)+b^2\beta(2,2)+\beta(3,3)+ab(\cos\gamma)\ B(1,2)+ac(\cos\beta)\ \beta(1,3)+bc(\cos\alpha)\ \beta(2,3)]$ where a,b,c are real cell parameters and $\beta(i,j)$ are anisotropic β's.

Table III. Some Bond Parameters for Dimeric Bridging Organo Imides of Uranium (IV).

Compound	a	b	c
U-N,Å	2.217(4)	2.156(8)	2.172(3)
U-N,Å	2.230(4)	2.315(8)	2.278(3)
ave.	2.22	2.24	2.23
U-N-C(Si), deg	129.7(2)	97.6(6)	113.9(2)
U-N-C(Si), deg	126.4(2)	157.1(7)	138.2(2)
ave.	128	127	126
U-N-U, deg	103.5(2)	104.7(4)	105.8(1)

a. $(MeC_5H_4)_4U_2(\mu\text{-}NSiMe_3)_2$

b. $(MeC_5H_4)_4U_2(\mu\text{-}NPh)_2$

c. $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(p\text{-tolyl})]_2$

Table IV. Some Bond Parameters (averaged values) in $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$ (a) and $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(p\text{-tolyl})]_2$ (b)

Compound	a	b
U-N (terminal), Å	2.339(8)	2.284(5)
U-N (bridging), Å	2.453(3)	2.172(3)
	2.646(3)	2.278(3)
N-U-N (terminal), deg	107.1(1)	109.1(1)

Table V. Magnetic Susceptibility Studies on $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$ (a) and $[(Me_3Si)_2N]_2U_2[\mu\text{-}N(p\text{-}tolyl)]_2$ (b).

	field strength[c]	T[d]	μ[e]	θ[d]
a	5	9-60	2.87	-22
	5	80-280	3.53	-71
	40	9-60	2.84	-22
	40	80-280	3.48	-66
b	5	5-40	4.37	-0.4
	5	160-280	3.34	+44
	40	5-40	4.91	-3
	40	160-280	3.39	+49

(c), in kgauss, (d) in deg. K, (e). the magnetic moment, μ is calculated as $\mu = 2.828C^{1/2}$ where C, the Curie Constant, is the reciprocal slope of the plot of $[\chi_M(corr)]^{-1}$ vs. T, see Figure III. Moments are expressed in Bohr magnetons per uranium. The χ_M (corr) values are corrected for container and sample diamagnetism.

Table VI. Crystal Data

	$[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$, a	$[(Me_3Si)_2N]_4U_2[\mu\text{-}N(p\text{-}tolyl)]_2$, b
Space Group	$P2_1/n$	$P\bar{1}$
a, Å	16.997(1)	9.792(1)
b, Å	11.854(1)	12.212(1)
c, Å	15.121(1)	14.580(3)
α, deg	90	62.00(1)
β, deg	99.10(1)	65.86(1)
γ, deg	90	80.80(1)
V, $Å^3$	3008(4)	1403.5(2)
Z	2	1
fw	1386.02	1327.90
d (calc.) g/cm^3	1.53	1.57
μ (calc.) cm^{-1}	52.85	56.61
radiation	MoKα (λ = 0.71073 Å)	
monochromator	highly oriented graphite	
scan. range, type	3° ≤ 2θ ≤ 45°, θ-2θ	
scan. speed, deg/min	0.84-6.7, variable	
scan. width, deg	Δθ = 0.65 + 0.35 tanθ	
reflections collected	4351; ±h, +k, +ℓ	3896; ±h, +k, ±ℓ
unique reflections	3932	3696
reflections, $F_o^2>3\sigma(F_o^2)$	3352	3451
R, %	1.98	1.83
R_w, %	2.55	2.77
R_{all}, %	3.48	2.24
GOF	1.695	1.580
g,e^{-2}	$1.30(3) \times 10^{-7}$	$4.6(1) \times 10^{-7}$
Largest Δ/σ in final least-square cycle	0.01	0.01
Temp (°C)	-75 ±4	-118 ±4

(a) Intensity Standards: -1, 8, -1; 4, 4, -9; -12, 1, -1; measured every hour of X-ray exposure time. Over the period of data collection there was a 1.7% decay in intensity.

(b) Intensity Standards: -6, -2, -7; -2, -7, -9; -2, -8, -3; measured every hour of X-ray exposure time. Over the period of data collection there was a negligible decay in intensity (< 1.0%).

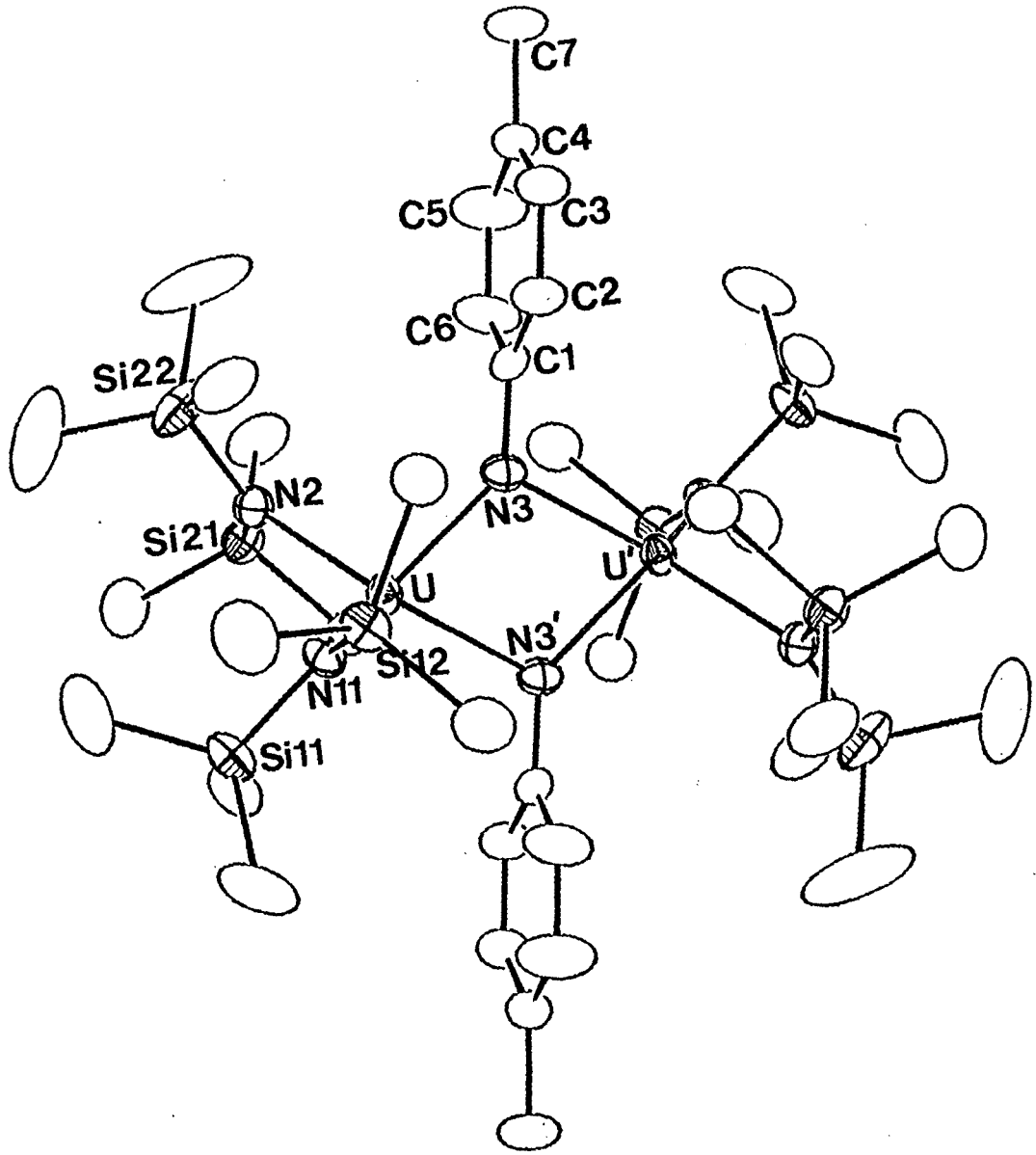
Orientation Standards: 3 reflections were checked after every 100 measurements. Crystal orientation was redetermined if any of the reflections were offset from their predicted positions by more than 0.1°. Reorientation was required seven times throughout the data collection. The cell constants listed were determined at the end of data collection.

Figure Captions

Figure I. ORTEP diagram of $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$, 50% probability ellipsoids except for the hydrogen atom on N(3) which is arbitrary; the hydrogen atom was found in the difference Fourier map but not refined. The primed and unprimed atoms are related by a crystallographic inversion center located in the center of the ring. U-N(1) = 2.354(3)Å, U-N(2) = 2.324(3)Å, U-N(3) = 2.453(3)Å, U-N(3') = 2.646(3)Å, N(3)-C(1) = 1.427(4)Å, N(1)-U-N(2) = 107.0(1)°, N(1)-U-N(3) = 112.9(1)°, N(1)-U-N(3') = 124.6(1)°, N(2)-U-N(3) = 103.5(1)°, N(2)-U-N(3') = 123.9(1)°, N(3)-U-N(3') = 77.2(1)°, U-N(3)-U' = 102.9(1)°, U-N(3)-C(1) = 135.8(2)°, U-N(3)-H = 103.0(2)°, U'-N(3)-C(1) = 94.3(2)°.

Figure II. ORTEP diagram of $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(p\text{-}tolyl)]_2$, 50% probability ellipsoids. The primed and unprimed atoms are related by a crystallographic inversion center located in the center of the ring. U-N(1) = 2.293(3)Å, U-N(2) = 2.274(2)Å, U-N(3) = 2.172(3)Å, U-N(3') = 2.278(3), N(3)-C(1) = 1.415(4)Å, N(1)-U-N(2) = 109.1(1)°, N(1)-U-N(3) = 114.8(1)°, N(1)-U-N(3') = 107.1(1)°, N(2)-U-N(3) = 100.9(1)°, N(2)-U-N(3') = 141.7(1)°, N(3)-U-N(3') = 74.2(1)°, U-N(3)-U' = 105.8(1)°, U-N(3)-C(1) = 138.2(2)°, U'-N(3)-C(1) = 113.9(2)°.

Figure III. Plot of χ_M^{-1} vs. T(K) for (a) $[(Me_3Si)_2N]_4U_2[\mu\text{-}N(H)(mesityl)]_2$. (b) $[(Me_3Si)_2N]_2U_2[\mu\text{-}N(p\text{-}tolyl)]_2$ at 5 kgauss field strength.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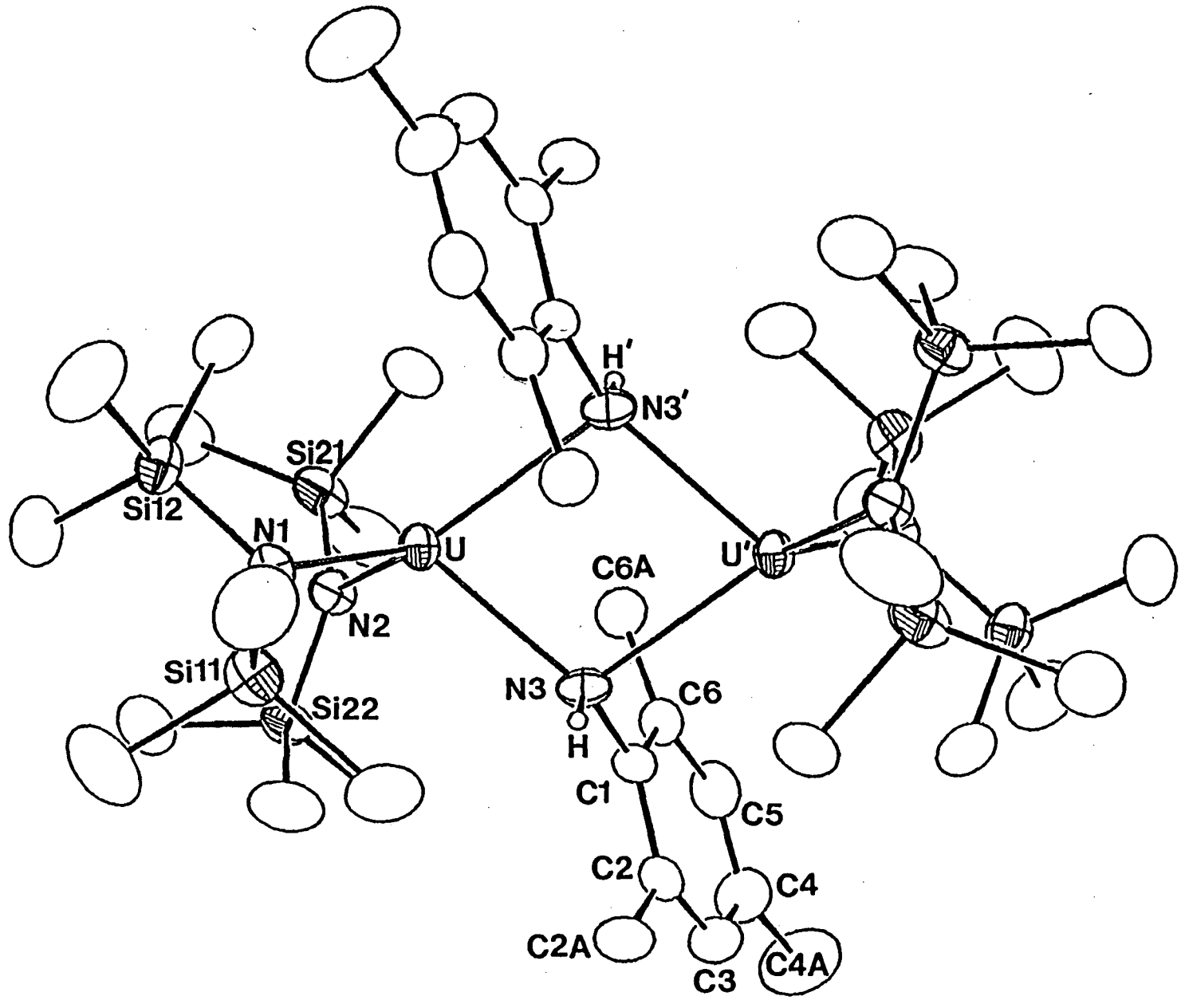
C4
C5
C3
C2
C6
C1
Si22
N2
N3
Si21
U
U'
N3'
Si12
N11
Si11


H'
N3'
Si21
Si12
N1
U
U'
C6A
N2
Si11
Si22
N3
C6
H
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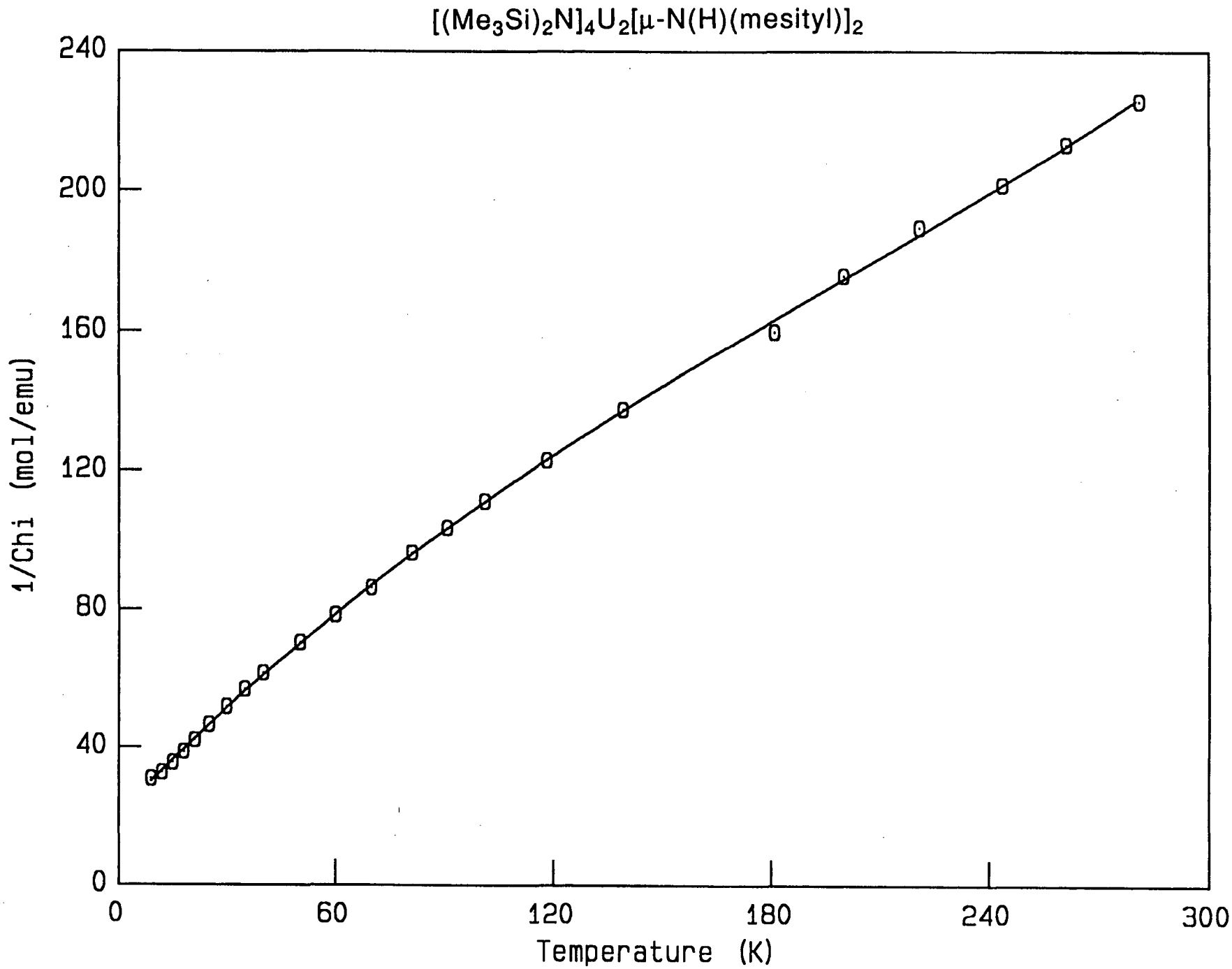
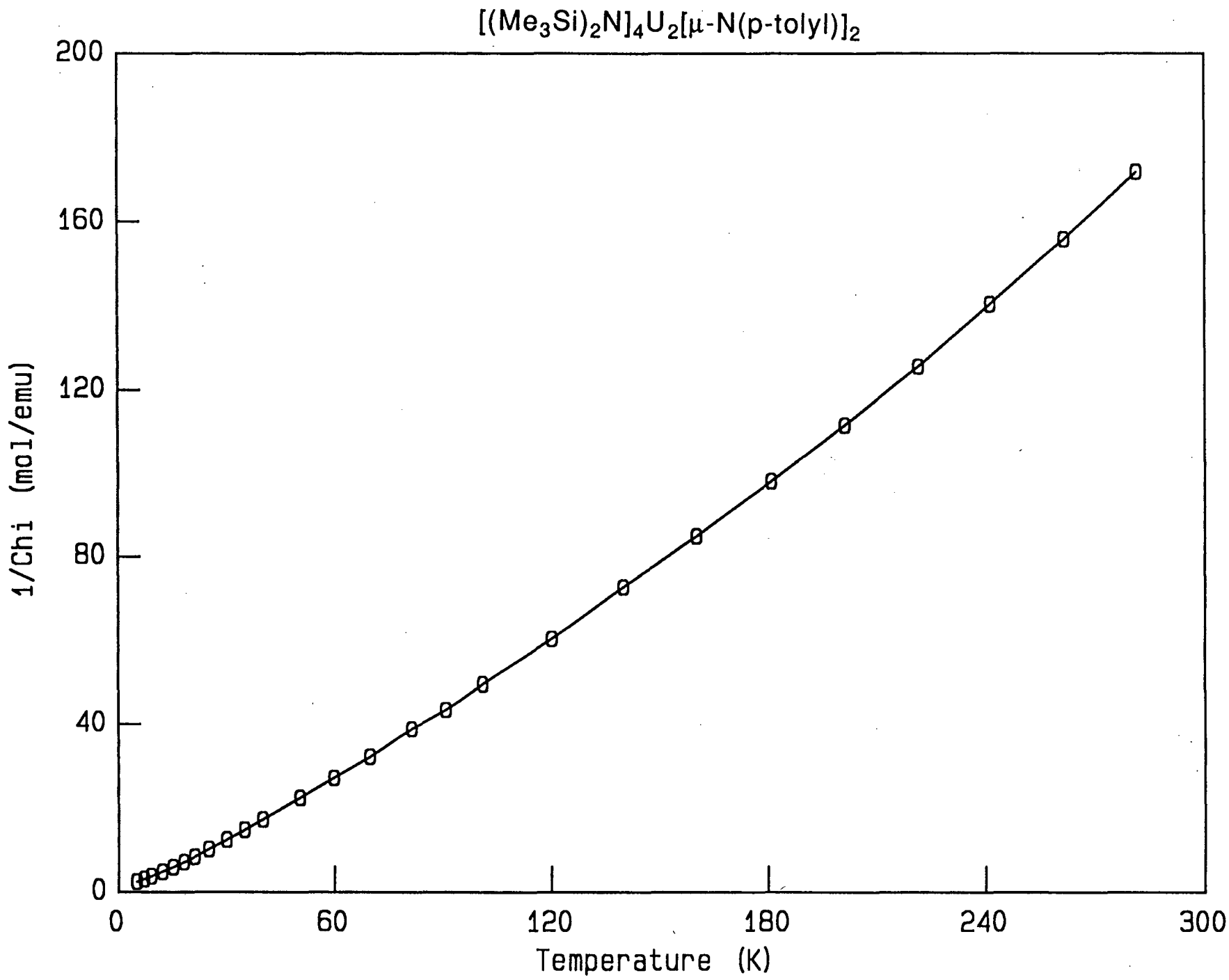
C4
C2A
C3
C4A


[(Me3Si)2N]4U2[μ-N(H)(mesityl)]2
240
200
160
120
80
40
0
1/Chi (mol/emu)
0
60
120
180
240
300
Temperature (K)


[(Me3Si)2N]4U2[μ-N(p-tolyl)]2
200
160
120
80
40
0
1/Chi (mol/emu)
0
60
120
180
240
300
Temperature (K)

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