UC-401
LBL-27499
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Submitted to Inorganic Chemistry

Trivalent Uranium Chemistry: Molecular Structure of $[(Me_3Si)_2N]_3U$

J.L. Stewart and R.A. Andersen

November 1989

For Reference
Not to be taken from this room

LBL-27499
Copy 1
Bldg. 50 Library.

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-27499

Trivalent Uranium Chemistry: Molecular Structure of $[(Me_3Si)_2N]_3U$

Joanne L. Stewart and Richard A. Andersen*

Department of Chemistry, University of California

and

Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory, Berkeley, California 94720

*Address all correspondence to this author at Chemistry Department, University of California, Berkeley, California 94720

The idealized geometry of binary, three-coordinate compounds, ML_3, is either trigonal planar (D_{3h} symmetry), pyramidal (C_{3v}) or T-shaped (C_{2v}). Molecular orbital models based upon Walsh diagrams,[1a,b] VSEPR concepts based upon electron pair repulsion,[1c] or a pure electrostatic model (the polarized-ion model)[1d,e] have been used to rationalize molecular geometry. The metal trihalides have been studied extensively at high temperature in gas phase[2a,b] and in solid state by matrix isolation spectroscopy.[2c] The principal difficulty in studies of molecules formed "under extreme" conditions is establishing the identity and constitution of the species under study; a recent article is particularly illuminating in this regard.[2d] One way around some of these problems is to prepare and isolate ML_3 compounds that can be shown to be pure, monomeric compounds by normal physical studies. This is a rather difficult task since three-coordinate molecules are coordinatively unsaturated and the compounds often exist in equilibrium among various species depending upon the phase, temperature, solvent, etc. One way to prevent molecular association is to use sterically bulky ligands. Many examples of the use of steric effects to prevent association are in the literature of ML_3 compounds.[3] A particularly illustrative example is found in organoaluminum chemistry; Me_3Al is a dimer in the solid state[4a,b], though its vapor is composed of monomer and dimer species.[4c] The organoaluminum compound with bulky groups, $(Me_3C)_3Al$, is a monomer under all conditions.[4d]

The bis(trimethylsilyl)amido ligand forms an extensive set of ML_2[5] and ML_3[6] compounds with the np, 3d, and 4f block metals. For $M[N(SiMe_3)_2]_3$ only monomeric compounds are known in the solid state and in gas phase though the geometry depends upon the phase. The p-block metals where M is Al, Ga, In, Tl are isostructural in the solid state with $P\bar{3}1c$ symmetry.[7] The molecules have trigonal planar geometry and their idealized symmetry is D_3 since the molecules are molecular propellars with the Me_3Si-blades giving the molecules a "handedness." In the first-row transition series where M is Ti, V, Cr, Mn, Fe, and Co the molecules are isostructural with the np-block metals and the

geometry is trigonal planar.[3,8] Compounds where M is Sc or the 4f-block metal, Nd, Eu, or Yb crystallize in the space group $P\bar{3}1c$ though the geometry is non-planar in each case.[3,9] The gas phase structures, where M is Ce, Pr, and La, have been determined by electron diffraction and these are also pyramidal.[10] Perhaps the most interesting example in the $[(Me_3Si)_2N]_3M$ series is that of scandium which is found to be pyramidal in solid state by X-ray diffraction[9b] though planar in gas phase by electron diffraction.[11]

Several years ago we prepared the silylamide derivative of the heaviest, naturally occurring element, uranium and showed that the molecule is monomeric in gas phase.[12] Though the solid state structure was not available, we suggested that the molecule was pyramidal on the basis of its infrared spectrum. In this paper we show that this deduction is correct.

Molecular Structure

An ORTEP diagram of $[(Me_3Si)_2N]_3U$ is shown in Figure I. Table I lists the crystal data. The molecule crystallizes in the space group $P\bar{3}1c$ as do all tris-silylamide metal compounds that have been crystallographically characterized. The uranium compound is pyramidal, and the uranium atom is disordered above and below the plane defined by the three nitrogen atoms by 0.456(1) Å. The U-N distance of 2.320(4) Å is unique though two comparisons may be made. The Nd-N and Ce-N distances in $[(Me_3Si)_2N]_3Nd$ in the solid state and $[(Me_3Si)_2N]_3Ce$ in the gaseous state are 2.29(2) Å[9c] and 2.33(4) Å,[10] respectively. The radii tabulated by Shannon[13] show that trivalent uranium in six coordination is 0.02 Å larger than trivalent cerium and 0.05 Å larger than neodymium. Extrapolation of these values gives a U-N distance of 2.34 or 2.35 Å, close to that observed.

The reason for the pyramidal geometry of $[(Me_3Si)_2N]_3U$ is not straightforward. The pyramidal geometry of $[(Me_3Si)_2N]_3M$, where M is Sc or Eu, was suggested to be due to the lack of M-N π-bonding in these compounds, the explicit deduction being that the

planarity of $[(Me_3Si)_2N]_3M$ was due to M-N π-bonding.[9b] A comprehensive study of the gas phase photoelectron spectroscopy of planar or pyramidal $[(Me_3Si)_2N]_3M$ compounds showed that the extent of M-N π-bonding in these compounds is insignificant.[14] Hence differential π-bonding cannot account for the change in geometry. Solid state packing forces are likely to be unimportant (except for scandium) since La, Ce, and Pr are pyramidal in the gaseous state[10] as are Nd[9c] and Eu[9b] in the solid state; the geometry of these 4f-block metals is pyramidal, regardless of physical state. A reasonable explanation for the pyramidal geometry found in the 4f-transition metal compounds is the polarized-ion model[10] and this model can be extended to $[(Me_3Si)_2N]_3U$.

In the polarized-ion model for ML_3 compounds, the geometry is largely determined by the size of the central ion and the size of the anionic ligands, L. Qualitatively, as the LML angle gets smaller than 120°, L···L repulsions will develop which will be destabilizing. For the smaller metals, i.e., those of the 3d-transition series, the planar geometry is determined largely by the L···L repulsions. As the metal ions get larger the intra-ligand repulsions become less destabilizing on bending and the pyramidal geometry is less unfavorable. In addition, bending LML away from 120° induces a dipole moment in the direction opposite of the bending. The interaction of the induced dipole moment with the negatively charged ligands is stabilizing (a charge-dipole interaction). Since the induced dipole moment is proportional to the polarizability which is proportional to the size of the metal ion, the largest ions should be the most pyramidal. This is consistent with the experimental facts.[10]

The polarized-ion model has been used to account for the non-linear geometry of gaseous BaF_2 in a quantitative way.[15] The model has been used in a qualitative way to relationalize the geometry and the thermodynamic properties of gaseous alkaline earth halides, oxides, and metallocenes.[1d, 16,17] An orbital hybridization model also has been used to explain the non-linear geometry of ML_2[18a,b] and the pyramidal geometry of ML_3[18c,d] compounds by including d-orbitals on the metal which will form molecular

orbitals with the ligand orbitals that are stabilized on bending. It is crucial to remember that the polarized-ion model is purely electrostatic and it allows electron exchange (covalency) by polarization whereas the molecular orbital model introduces polarization by including d-orbitals. Both models account for the experimental facts and arguments over which model is to be preferred is largely governed by the intuitive and subjective view of how "ionic" or how "covalent" one thinks that the bonds are. One's intuition is largely determined by the ideas of relative orbital energies and how these are related to electronegativity. Indeed these arguments are largely semantic since in molecular orbita calculations d-orbitals are polarization functions and polarization is invoked to rationalize bending in the ionic model, hence the equivalent answer is obtained from either extreme bond model. In this content it is useful to quote from the second edition of Cotton and Wilkinson "covalent bonding can be considered as a case of ionic bonding in which polarization of the anions is so extreme as to give an appreciable increase in electron density between the nuclei. Although this view is severely limited insofar as quantitative treatment is concerned, and is not in general a substitute for the quantum mechanical treatment of covalent bonding, it has certain merits as an approach to bonds that are mainly ionic, with a little covalence."[19]

Magnetic Susceptibility

The plot of the inverse susceptibility as a function of temperature for $[(Me_3Si)_2N]_3U$ is shown in Figure II. The magnetic moment (μ_B) is 3.354(4) B.M. (θ = -13K) at 5 kGauss and 3.385(4) B.M. (θ = -11K) at 40 kGauss over the temperature range of 35-280K. The shape of the curve and the magnetic moment are similar to those previously reported for other trivalent uranium compounds.[20,22] Some controversy surrounds the ground state electronic structure of trivalent uranium metallocenes. A theoretical paper has appeared recently which suggests that the ground state electronic structure of Cp_3U is not $5f^3$ but rather $6d^15f^2$.[21] We have shown that the above mentioned theory leads to the incorrect answer, since the magnetic susceptibility, optical, and EPR

studies show that the monomeric metallocenes $(Me_3SiC_5H_4)_3U$, $[(Me_3Si)_2C_5H_3]_3,U$ and their coordination complexes have a $5f^3$ electronic ground state.[22] The similarity in the shape of the plot of inverse susceptibility as a function of temperature for $[(Me_3Si)_2N]_3U$, Figure II, and that of $[(Me_3Si)_2C_5H_3]_3U$ and $[(Me_3Si)C_5H_4]_3U(CNCMe_3)$[22] strongly support the contention that these three molecules are isoelectronic In addition, the shape of the curve in Figure II is similar to that for UF_3 from 5-300K which gives a magnetic moment of 3.66 B.M. over a temperature range of 125-300K.[23] The similarity of the optical spectra[20c,22] and magnetic susceptibility results for this wide range of trivalent uranium compounds strongly supports the contention that they have the same ground state electronic structure as that found in U(III) in $LaCl_3$, viz. $5f^3$.[24]

Experimental Section

The silylamide, $[(Me_3Si)_2N]_3U$, was prepared as previously described.[12] The infrared spectrum and melting point was identical to that previously reported but the ^1H NMR spectrum (20°, C_6D_6) is a singlet at δ-11.4 ($\nu_{1/2}$ = 15 Hz) rather than at -18.1 as previously reported.

X-ray Crystallography of $[(Me_3Si)_2N]_3U\cdot\frac{1}{3}(C_6H_{12})$

Deep purple crystals of the compound were obtained by slow cooling of a saturated cyclohexane solution to -15°C. Crystals of appropriate size were mounted in 0.3 mm thin-walled quartz capillaries in an inert-atmosphere glove box. The capillaries were removed from the box and flame sealed. Preliminary precession photographs indicated trigonal Laue symmetry and yielded preliminary cell dimensions.

The crystal used for data collection was of approximate dimensions 0.39 mm × 0.20 mm × 0.20 mm. It was transferred to an Enraf-Nonius CAD-4 diffractometer and cooled to -110°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 Laue symmetry as the precession photographs and systematic absences indicated the space group to be either P31c or $P\bar{3}1c$. The normalized structure factor statistics suggested the choice of the acentric space group, however, a successful solution in the acentric group could not be achieved. A successful solution was found using the space group $P\bar{3}1c$. The final cell parameters and specific data collection parameters are given in Table II.

The 1886 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 (1.4%) during data collection. Inspection of the azimuthal scan data showed a variation $I_{min}/I_{max} = 0.90$ for the average curve. An empirical correction for absorption, based on the azimuthal scan data, was applied to the intensities. Removal of systematically absent data and averaging of redundant data left 905 unique data. The redundant data were averaged with an agreement factor, based on F_{obs}, of 1.5% for observed and accepted data and 3.9% for all data.

The structure was solved by Patterson methods and refined via 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, as well as a large peak near the origin, vide infra. 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 1.15 $Å^2$ larger than the equivalent B_{iso} of the atom to which they were bonded. None of the hydrogens were refined in least squares.

After the hydrogen atoms were included in the structure, a model for the electron density near the origin was developed. Hursthouse and Rodesiler found that $Fe[N(SiMe_3)_2]_3$ crystallized with a channel running down the z-axis that is large enough to accommodate a benzene molecule.[8d] Successful refinement of solvent molecules in the channel has not been achieved in any of the tris(bis(trimethylsilyl)amido)metal structures. In $[(Me_3Si)_2N]_3U$, the large peak near the origin in the difference Fourier map was able to be refined with anisotropic thermal parameters as a carbon atom with 1/3 occupancy. The symmetry generated positions gave reasonable bond lengths and angles that showed the atom to be part of a disordered cyclohexane ring. The hydrogen atoms of the cyclohexane molecule were not included. The thermal parameters showed the carbon atom to be severely anisotropic: B(1,1) = 4.7(6), B(2,2) = 3.7(5), B(3,3) = 19(1), with the motion (or disorder) in the z-direction. This model accounted nicely for the electron density found in the channel and the largest peaks in the final difference Fourier map are now associated with the uranium and are not found in the channel. A packing diagram, that shows the C_6H_{12} molecule is in the Supplementary Material.

The quantity minimized by the least squares was $\Sigma w(|F_o|-|F_c|)^2$, where w is the weight of a given observation. The p-factor, used to reduce the weight of intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

Inspection of the residuals ordered in ranges of $\sin(\theta/\lambda)$, $|F_o|$, and parity and value of the individual indices showed no unusual features or trends. A secondary extinction parameter was refined in the final cycles of least squares. Seven reflections were rejected as "bad" data in the final refinement, based on their high values of $w \times \Delta^2$. The highest and lowest peaks in the final difference Fourier map had electron densities of 0.364 and -0.215 $e^{-1}/Å^3$, respectively, and were associated with the uranium atom.

Acknowledgement. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. We thank Dr. F.J. Hollander, staff crystallographer of the University of California, Berkeley CHEXRAY facility for his help with the X-ray crystallography.

References

1. (a) Burdett, J.K. "Molecular Shapes" Wiley, New York, 1980. (b) Albright, T.A.; Burdett, J.K.; Whangbo, M.H. "Orbital Interactions in Chemistry" Wiley, New York, 1985. (c) Gillespie, R.J. "Molecular Geometry", Van Nostrand-Rheinhold, London, 1972. (d) Drake, M.C.; Rosenblatt, G.M. J. Electrochem. Soc. **1979**, 126, 1387. (e) Hildenbrand, D.L. Ibid. **1979**, 126, 1396.
2. (a) Hargittai, M. Coord. Chem. Rev. **1988**, 91, 35. (b) Hargittai, M. in "Stereochemical Applications of Gas-Phase Electron Diffraction" Hargittai, I. (ed.) VCH Publishers, Part B, 1988, p. 383 (c) Nakamoto, K. "Infrared and Raman Spectra" Wiley, New York, 4th ed. 1986, p. 108. (d) Beattie, I.R.; Jones, P.J.; Young, N.A. Angew. Chem. Int. Ed. **1989**, 28, 313.
3. Eller, P.G.; Bradley, D.C.; Hursthouse, M.B.; Meek, D.W. Coord. Chem. Rev. **1977**, 24, 1.
4. (a) Rundle, R.E. J. Am. Chem. Soc. **1947**, 69, 1327. (b) Hoffman, J.C.; Streib, W.E. J. Chem. Soc. Chem. Comm. **1971**, 911. (c) Almenningen, A.; Halvorsen, S.; Haaland, A. Acta Chem. Scand. **1971**, 25, 1937. (d) Lehmkuhl, H.; Olbrysch, O.; Nehl, H. Annalen. **1973**, 708.
5. Power, P.P. Comments Inorg. Chem. **1989**, 8, 177.
6. Lappert, M.F.; Power, P.P.; Sanger, A.R.; Srivastava, R.C. "Metals and Metalloid Amides" Ellis Horwood, Chichester, 1980.
7. (a) Pump, J.; Rochow, E.G.; Wannagat, U. Angew. Chem. Int. Ed. **1963**, 2, 264. (b) Bürger, H.; Chicon, J.; Goetze, U.; Wannagat, U.; Wismar, H.J. J. Organomet. Chem. **1971**, 33, 1. (c) Krommes, P.; Lorberth, J. Ibid. **1977**, 131, 415. (d) Sheldrick, G.M.; Sheldrick, W.S. J. Chem. Soc. (A) **1969**, 2279. (e) Allman, R.; Henke, W.; Krommes, P.; Lorberth, J. J. Organomet. Chem. **1978**, 162, 283.

8. (a) Bürger, H.; Wannagat, U. Monatsh. Chem. **1963**, 94, 1007. (b) Bürger, H.; Wannagat, U. Ibid. **1964**, 95, 1099. (c) Alyea, E.C.; Bradley, D.C.; Copperthwaite, R.G. J. Chem. Soc. Dalton Trans. **1972**, 1580. (d) Hursthouse, M.B.; Rodesiler, P.F. Ibid. **1972**, 2100. (e) Ellison, J.J.; Power, P.P.; Schoner, S.C. J. Am. Chem. Soc. **1989**, 111, 8044.

9. (a) Bradley, D.C.; Ghotra, J.S.; Hart, F.A. J. Chem. Soc. Dalton Trans. **1973**, 1021. (b) Ghotra, J.S.; Hursthouse, M.B.; Welch, A.J. J. Chem. Soc. Chem. Comm. **1973**, 669. (c) Andersen, R.A.; Templeton, D.H.; Zalkin, A. Inorg. Chem. **1978**, 17, 2317.

10. Fjeldberg, T.; Andersen, R.A. J. Mol. Struct. **1985**, 129, 93.

11. Fjeldberg, T.; Andersen, R.A. J. Mol. Struct. **1985**, 128, 49.

12. Andersen, R.A. Inorg. Chem. **1979**, 18, 1507.

13. Shannon, R.D. Acta Cryst. **1976**, 32A, 751.

14. Green, J.C.; Payne, M.; Seddon, E.A.; Andersen, R.A. J. Chem. Soc. Dalton Trans. **1982**, 887.

15. Guido, M.; Gigli, G. J. Chem. Phys. **1976**, 65, 1397.

16. (a) Guido, M.; Gigli, G. J. Chem. Phys. **1974**, 61, 4138. (b) Hildenbrand, D.L. J. Electrochem. Soc. **1979**, 126, 1396.

17. (a) Andersen, R.A.; Boncella, J.M.; Burns, C.J.; Green, J.C.; Hohl, D.; Rösch, N. J. Chem. Soc. Chem. Comm. **1986**, 405. (b) Andersen, R.A.; Blom, R.; Burns, C.J.; Volden, H.V. Ibid. **1987**, 768. (c) Andersen, R.A.; Boncella, J.M.; Burns, C.J.; Blom, R.; Haaland, A.; Volden, H.V. J. Organomet. Chem. **1986**, 312, C49. (d) Andersen, R.A.; Blom, R.; Boncella, J.M.; Burns, C.J.; Volden, H.V. Acta Chem. Scand. **1987**, 41A, 24. (e) Green, J.C.; Hohl, D.; Rösch, N. Organometallics, **1987**, 6, 712. (f) Blom, R.; Faegri, K.; Volden, H.V. Ibid. in press.

18. (a) Hayes, E.F. J. Phys. Chem. **1966**, 70, 3740. (b) Coulson, C.A. Isr. J. Chem. **1973**, 11, 683. (c) Meyers, C.E.; Norman, L.J.; Loew, L.M. Inorg. Chem. **1978**, 17, 1581. (d) Ruscic, B.; Goodman, G.L.; Berkowitz, J. J. Chem. Phys. **1983**, 78, 5443.

19. Cotton, F.A.; Wilkinson, G. "Advanced Inorganic Chemistry," Wiley, New York, 2nd ed., 1966, p.54.

20. (a) Kanellakopulos, B. in "Organometallics of the f-Elements," Marks, T.J.; Fischer, R.D. (eds.) D. Reidel, Dordrecht, 1979, p. 1. (b) Kanellakopulos, B. in "Gmelin Handbuch der Anorganische Chemie" Uranium Suppl. A.6, 1983, p.1. (c) Kanellakopulos, B.; Fischer, E.O.; Dornberger, E.; Baumgärtner, F. J. Organomet. Chem. **1970**, 24, 507.

21. Bursten, B.E.; Rhodes, L.F.; Strittmatter, R.J. J. Am. Chem. Soc. **1989**, 111, 2756.

22. Beshouri, S.M.; Andersen, R.A.; Edelstein, N.M. to be submitted.

23. Berger, M.; Sienko, M.J. J. Organomet. Chem. **1967**, 6, 324.

Table I. Positional Parameters for $[(Me_3Si)_2N]_3U \cdot \frac{1}{3}(C_6H_{12})$

Atom	x	y	z	B(Å^2)
U	0.333	0.667	0.19511(5)	2.482(8)
Si	0.54890(6)	0.83491(6)	0.3896(1)	2.47(2)
N	0.4938(3)	0.747	0.250	2.20(9)
C1	0.6452(3)	0.8296(3)	0.5025(6)	4.6(1)
C2	0.4581(3)	0.8220(3)	0.5409(4)	3.8(1)
C3	0.5999(3)	0.9551(3)	0.2988(5)	4.0(1)
C4	0.091(1)	0.092(1)	0.238(3)	9.1(5)
H1a	0.6925	0.8359	0.4291	5.3*
H1b	0.6719	0.8794	0.5790	5.3*
H1c	0.6198	0.7707	0.5567	5.3*
H2a	0.4307	0.7614	0.5892	4.3*
H2b	0.4871	0.8691	0.6214	4.3*
H2c	0.4103	0.8289	0.4884	4.3*
H3a	0.5523	0.9595	0.2407	4.6*
H3b	0.6237	1.0012	0.3818	4.6*
H3c	0.6497	0.9656	0.2276	4.6*

*Atoms were included with isotropic thermal parameters. The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as: (4/3) $[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ where a,b,c are real cell parameters, and B(i,j) are anisotropic β. The atom labelled as C4 is the disordered cyclohexane molecule of crystallization, see Experimental Section for details.

Table II. Crystal Data for $U[N(SiMe_3)_2]_3 \cdot 1/3(C_6H_{12})$ (-110±4°C)

Space Group	$P\bar{3}1c$
a, b, Å	16.370(2)
c, Å	8.302(1)
α, deg	90
β, deg	90
γ, deg	120
V, $Å^3$	1926.7(1)
Z	2
fw	719.20
d (calc.) g/cm^3	1.26
μ (calc.) 1/cm	41.88
radiation	MoKα (λ = 0.71073Å)
monochromator	highly oriented graphite
scan range, type	$3° \leq 2\theta \leq 45°$, θ-2θ
scan speed, deg/min	0.84-6.7, variable
scan width, deg	$\Delta\theta = 0.60 + 0.35 \tan\theta$
reflections collected	1886; +h, +k, ±1
unique reflections	845
reflections, $F_o^2 > 3\sigma(F_o^2)$	654
R, %	2.17
R_w, %	2.90
R_{all}, %	4.95
GOF	1.267
g, e^{-2}	$1.7(3) \times 10^{-7}$
Largest Δ/σ in final least-square cycle	0.02

Intensity Standards: 4, 4, -4; 11, -5, -1; -5, 11, 1; measured every hour of X-ray exposure time. Over the period of data collection there was a 1.4% decay in intensity.

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 once throughout the data collection. The cell constants listed were determined at the end of data collection.

Figure Captions

Figure I. ORTEP diagram, down the $\bar{3}$-axis of $[(Me_3Si)_2N]_3U\cdot\frac{1}{3}(C_6H_{12})$ at -110°C, 50% thermal ellipsoids, showing one of the two disordered uranium sites. U-N = 2.320(4) Å, N-Si = 1.713(1) Å, N-U-N = 116.24(7)°, Si-N-Si = 125.8(2)°.

Figure II. Plot of inverse magnetic susceptibility vs. temperature (K) for $[(Me_3Si)_2N]_3U$, the top curve is the values at a field strength of 5 kGauss, the bottom at 40 kGauss.

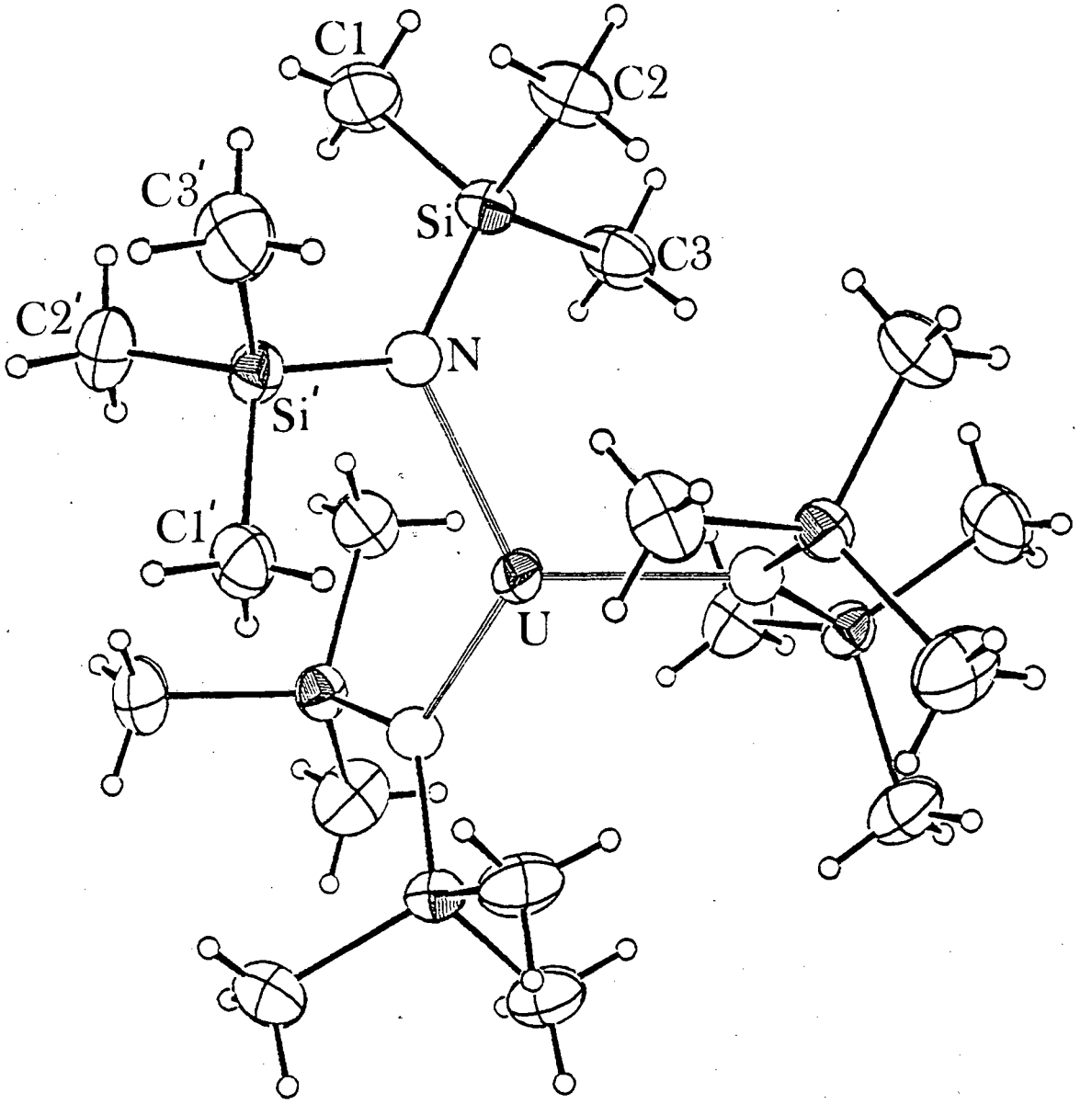
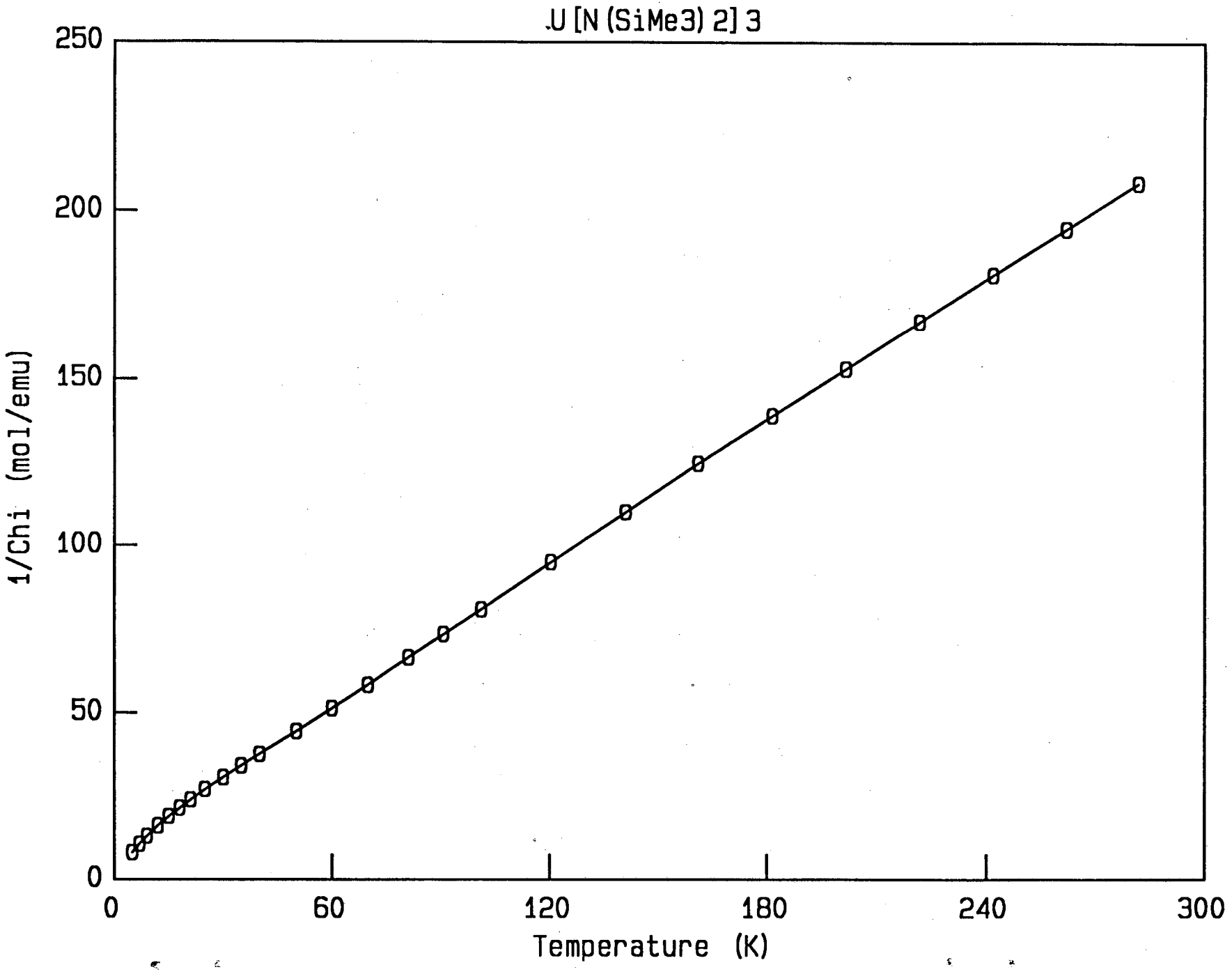


Figure I.


.U [N (SiMe3) 2] 3
250
200
150
100
50
0
1/Chi (mol/emu)
0
60
120
180
240
300
Temperature (K)

Supplementary Material Available for

Trivalent Uranium Chemistry: Molecular Structure of $[(Me_3Si)_2N]_3U$

Joanne L. Stewart and Richard A. Andersen

Tables bond lengths and angles, anisotropic thermal parameters, structure factor tables, and a packing diagram showing the disordered C_6H_{12}. Ordering information is given on any current masthead page.

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720