

Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and the Department of Chemistry, University of California, Berkeley, California 94720

Preparation and Crystal Structure of Uranium(IV) Borohydride-*n*-Propyl Ether¹

ALLAN ZALKIN,* RICHARD R. RIETZ, DAVID H. TEMPLETON,* and NORMAN M. EDELSTEIN*

Received July 27, 1977

Uranium(IV) borohydride reacts with di-*n*-propyl ether to form $U(BH_4)_4 \cdot O(n-C_3H_7)_2$, a light green solid that can be sublimed at 30–40 °C and 10^{-5} mm. Structural characterization by single-crystal x-ray diffractometry has shown the molecule to contain two uranium atoms in different environments. One uranium atom is bonded to oxygen of two ether molecules and via 11 hydrogen atoms to 4 borohydride ions. The other uranium has 14 hydrogen neighbors from 5 borohydride ions, one of which acts as a bridge to the first uranium atom. This unsymmetrical dimer is in marked contrast to the linear polymeric chain structures of $U(BH_4)_4 \cdot O(CH_3)_2$ and $U(BH_4)_4 \cdot O(C_2H_5)_2$. The propyl compound is triclinic, space group $P\bar{1}$, with $a = 12.043(10)$ Å, $b = 10.340(8)$ Å, $c = 14.752(13)$ Å, $\alpha = 82.81(5)^\circ$, $\beta = 112.99(5)^\circ$, $\gamma = 110.76(5)^\circ$, $Z = 4$, and $d_{\text{calc}} = 1.68$ g cm⁻³ at 22 °C. $R = 0.063$ for 833 reflections, with $I > 3\sigma$ and with restraints on the bond distances and some of the bond angles.

Introduction

In our study of Lewis-base adducts of uranium(IV) borohydride,² we have discovered a number of volatile etherates. Structural characterization of two of these compounds,³ $U(BH_4)_4 \cdot O(CH_3)_2$ and $U(BH_4)_4 \cdot O(C_2H_5)_2$, has shown them to be linear polymers in the crystalline state. The complex with tetrahydrofuran is a dietherate and is monomeric in the crystalline state.⁴

When $U(BH_4)_4$ and di-*n*-propyl ether were allowed to react, a light green solid was formed that sublimed at room temperature (20 °C), some 20 °C lower than the sublimation temperature for the dimethyl or diethyl etherates. This unexpected increase in volatility with increased molecular weight prompted us to examine the crystal and molecular structure of this solid.

Experimental Section

Materials and Chemical Techniques. $U(BH_4)_4$ was prepared by the method of Schlesinger and Brown⁵ and purified by sublimation at 30–40 °C and 10^{-5} mm. Di-*n*-propyl ether (Aldrich) was distilled from sodium/benzophenone under argon and then redistilled from $LiAlH_4$ under vacuum. All manipulations were performed in Pyrex high-vacuum lines free of mercury, oil, and grease or in argon-filled dryboxes.⁶

Preparation of $[U(BH_4)_4 \cdot O(n-C_3H_7)_2]_2$. In a typical preparation, 0.63 g $U(BH_4)_4$ (2.12 mmol) was sublimed to a 100-mL trap at -78 °C. Di-*n*-propyl ether (2.61 g) was condensed on top of the $U(BH_4)_4$. The trap was sealed, removed from the vacuum line, and shaken occasionally as it warmed to room temperature (~1 h). A deep green solution formed as the $U(BH_4)_4$ dissolved. There were no intermediate colors. The trap was cooled to 0 °C and reattached to the vacuum line. Excess $(n-C_3H_7)_2O$ was removed by pumping for 30 min. Retained was 0.22 g of $(n-C_3H_7)_2O$ (2.15 mmol), or 1.015 ethers per borohydride. The light green crystals were pumped without heating to a tared trap at -78 °C. The yield was quantitative, 0.85 g (2.13 mmol), based on the empirical formula; mp 62–63 °C (sealed capillary). This compound decomposes very slowly over a period of several months under vacuum or under argon. Additional physical and spectroscopic data will appear elsewhere.²

On standing in sealed capillaries for a few months, the crystals changed to a red color, and the structure was determined for this red material. A powder diffraction pattern taken with the fresh green crystals corresponds to the single-crystal results in its line positions and qualitative intensities. A similar color change from green to red, without a change of crystal structure, was observed for both the methyl and the ethyl adducts of uranium borohydride when they were exposed to x rays.³

Crystal Growth. Attempts to manipulate individual crystals in an argon drybox met with repeated failures, mainly due to mechanical destruction or distortion of the crystals. Instead, several crystals were shaken into a capillary drawn from a 14/35 quartz joint. The remaining operations for crystal growth have been described previously.⁴

X-Ray Diffraction. Several of the small red crystals were investigated, and finally a small crystal about $0.09 \times 0.11 \times 0.06$ mm was selected and placed on a Picker FACS-I automatic diffractometer

equipped with a graphite monochromator and a Mo anode x-ray tube, $\lambda(K\alpha_1)$ 0.709 26 Å. The crystal was found to have a triclinic cell. Twelve reflections between 20 and 25° of 2θ were carefully centered, and a least-squares refinement of the lattice dimensions based on the setting angles gave $a = 12.043(10)$ Å, $b = 10.340(8)$ Å, $c = 14.752(13)$ Å, $\alpha = 82.81(5)^\circ$, $\beta = 112.99(5)^\circ$, and $\gamma = 110.76(5)^\circ$, at 22 °C. The unit cell volume was 1580 Å³, and for $Z = 4$, the calculated density was 1.68 g cm⁻³; the space group is $P\bar{1}$. ω scans of the three reflections 001, 010, and 200 had widths at half-peak height of 0.11, 0.10, and 0.14°, respectively, and after 128 h of data-taking these values had increased to 0.35, 0.35, and 0.40°.

Using the θ - 2θ scan technique, 4480 reflections, including standards, were collected. The three standard reflections, 200, 1 $\bar{2}$ 1 and 1 $\bar{0}$ 5, were measured after each 200th scan; at the termination of the data collection they were 74, 73, and 67% of their initial values, respectively.

The scan speed was 1°/min along 2θ for the first 1332 data, but when the rapid decay of the crystal was evident, this was increased to 2°/min to accelerate the data collection. The scan width was 1.4° plus the amount of the $K\alpha_1$ - $K\alpha_2$ divergence, and this was increased to 1.6° and then to 1.8° as the crystal decay broadened the peaks. Backgrounds were taken at 0.5° before and after the scan limits. A full sphere of data to 35° in 2θ were collected.

A decay correction was applied to the intensities based on an average of the approximately linear decay of the three standards. The absorption factor μ was calculated as 98 cm⁻¹, but no absorption correction was made because the crystal faces were too indistinct to be measured and identified through a distorting and uneven quartz capillary. The data reduction and assignment of standard deviations were according to the formulas given in the supplementary material. The "ignorance factor" p was 0.06. Of the 2026 unique data, only 880 had intensities greater than 3σ .

A three-dimensional Patterson-function map revealed the positions of the two uranium atoms in the asymmetric unit. A series of Fourier maps, least-squares refinement, and difference-Fourier maps were calculated, and from these the full structure was determined. Although the structure could be recognized in the Fourier maps, the light-atom peaks were poorly resolved and smeared. This is attributable both to the lack of high-angle data, i.e., no data above 35° of 2θ , and to the low quality of data caused by the crystal decay and the lack of an absorption correction. Least-squares refinement of this structure converged to give coordinates and bond distances (listed in the supplementary material), some of which were inconsistent with reasonable values. One boron atom, B(1), was between the two uranium atoms, and we assumed it to share two hydrogen atoms with each of them. The other boron atoms each had only one uranium neighbor, and these terminal borohydride ions were each assumed to have three of their hydrogen atoms bonded to uranium. In further refinement we imposed restraints on interatomic distances according to the Waser method,⁷ which is as follows. Interatomic distances between selected atoms are introduced into the least-squares calculations and treated as observations; estimated standard deviations of these distances are also introduced and used to calculate the weights. Except that the derivatives of these distances with respect to the positional parameters are calculated by a special patch and that these "observations" are not included in the R values reported here, these terms are included in the least-squares calculation in the same manner as observed structure factors. This procedure allows the structure

Table I. Positional Parameters with Estimated Standard Deviations^a for U(BH₄)₄·O(C₃H₇)₂

| Atom | x | y | z |
|-------|------------|------------|------------|
| U(1) | 0.7659 (3) | 0.0599 (3) | 0.2744 (2) |
| U(2) | 0.3447 (3) | 0.2569 (3) | 0.1705 (2) |
| O(1) | 0.844 (3) | 0.263 (3) | 0.179 (2) |
| O(2) | 0.679 (4) | -0.139 (4) | 0.369 (3) |
| B(1) | 0.538 (8) | 0.13 (1) | 0.221 (9) |
| B(2) | 0.968 (8) | 0.01 (1) | 0.333 (9) |
| B(3) | 0.636 (7) | 0.928 (8) | 0.111 (4) |
| B(4) | 0.842 (8) | 0.206 (7) | 0.424 (4) |
| B(5) | 0.228 (8) | 0.010 (6) | 0.203 (7) |
| B(6) | 0.516 (6) | 0.461 (6) | 0.137 (5) |
| B(7) | 0.322 (9) | 0.381 (9) | 0.296 (6) |
| B(8) | 0.18 (1) | 0.27 (2) | 0.007 (6) |
| C(1) | 0.763 (8) | 0.294 (9) | 0.082 (4) |
| C(2) | 0.832 (8) | 0.27 (1) | 0.018 (6) |
| C(3) | 0.757 (9) | 0.31 (1) | -0.086 (6) |
| C(4) | 0.96 (1) | 0.38 (1) | 0.22 (1) |
| C(5) | 1.01 (2) | 0.54 (1) | 0.23 (1) |
| C(6) | 0.96 (1) | 0.60 (1) | 0.28 (1) |
| C(7) | 0.678 (8) | -0.280 (7) | 0.350 (6) |
| C(8) | 0.778 (8) | -0.296 (7) | 0.449 (6) |
| C(9) | 0.79 (1) | -0.436 (9) | 0.433 (8) |
| C(10) | 0.612 (7) | -0.135 (8) | 0.434 (5) |
| C(11) | 0.474 (8) | -0.220 (9) | 0.385 (6) |
| C(12) | 0.393 (9) | -0.21 (1) | 0.441 (8) |

^a Here and in the following tables the number in parentheses is the standard deviation in the least significant digit estimated by least-squares refinement on a model with most of the light-atom distances restrained.

Table II. Interatomic Distances (Å)

| | | | |
|-----------|----------|-------------|----------|
| U(1)-O(1) | 2.48 (4) | O(1)-C(1) | 1.46 (5) |
| -O(2) | 2.48 (4) | -C(4) | 1.46 (6) |
| -B(1) | 2.90 (4) | O(2)-C(7) | 1.52 (5) |
| -B(2) | 2.49 (6) | -C(10) | 1.48 (5) |
| -B(3) | 2.55 (5) | C(1)-C(2) | 1.56 (5) |
| -B(4) | 2.50 (5) | C(2)-C(3) | 1.50 (5) |
| U(2)-B(1) | 2.84 (5) | C(4)-C(5) | 1.49 (6) |
| -B(5) | 2.53 (5) | C(5)-C(6) | 1.49 (6) |
| -B(6) | 2.53 (5) | C(7)-C(8) | 1.52 (5) |
| -B(7) | 2.53 (5) | C(8)-C(9) | 1.59 (5) |
| -B(8) | 2.49 (6) | C(10)-C(11) | 1.50 (5) |
| | | C(11)-C(12) | 1.54 (6) |

to adjust to the electron density with a flexibility governed by the weighting. The following restraints were imposed: U-B(bridge) 2.89 ± 0.05 Å, U-B(terminal) 2.49 ± 0.05 Å, U-O 2.52 ± 0.05 Å, O-C 1.47 ± 0.05 Å, C-C (first neighbor) 1.52 ± 0.05 Å, and C-C (second neighbor) 2.48 ± 0.08 Å. The propyl groups are thus restrained to tetrahedral bond angles but are allowed to rotate about the O-C bonds. Anisotropic thermal parameters were applied to the uranium atoms only. The structure was refined by full-matrix least squares where the function $\sum w(\Delta F)^2 / \sum w F_o^2$ was minimized. The scattering factors used were those of Doyle and Turner⁸ for the neutral light atoms and those of Cromer and Waber⁹ for the uranium atom corrected for dispersion according to Cromer and Liberman.¹⁰ All 48 data below $(\sin \theta) / \lambda$ of 0.13 were deleted because of their large discrepancies; this is in the region of enhanced background due to the quartz-capillary scattering and where the absorption errors are most serious. The discrepancy indices for 833 data, where $I > 3\sigma$, are

$$R = \sum |F_o| - |F_c| / \sum |F_o| = 0.063$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2} = 0.066.$$

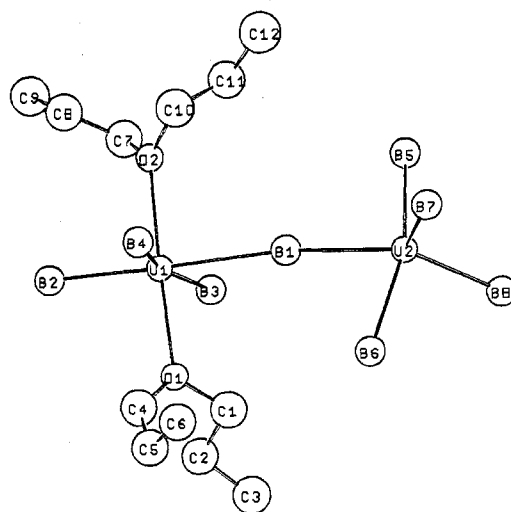
The estimated error in an observation of unit weight is 1.30. In the last cycle, no parameter shifted more than 0.1σ.

Results and Discussion

Atomic coordinates are given in Table I. Tables II and III give some distances and angles, and Figure 1 shows the molecular structure. The structure is an unsymmetrical dimer of two formula units in which two uranium atoms are bridged by a borohydride unit. One of the uranium atoms is at the center of an irregular octahedron consisting of two *n*-propyl

Table III. Selected Angles (deg)

| | | | |
|----------------|---------|-------------------|---------|
| O(1)-U(1)-O(2) | 177 (2) | B(1)-U(2)-B(5) | 78 (3) |
| O(1)-U(1)-B(1) | 87 (3) | B(1)-U(2)-B(6) | 81 (3) |
| O(1)-U(1)-B(2) | 94 (3) | B(1)-U(2)-B(7) | 122 (3) |
| O(1)-U(1)-B(3) | 87 (2) | B(1)-U(2)-B(8) | 129 (4) |
| O(1)-U(1)-B(4) | 92 (2) | B(5)-U(2)-B(6) | 159 (3) |
| O(2)-U(1)-B(1) | 90 (3) | B(5)-U(2)-B(7) | 100 (3) |
| O(2)-U(1)-B(2) | 89 (3) | B(5)-U(2)-B(8) | 96 (4) |
| O(2)-U(1)-B(3) | 93 (2) | B(6)-U(2)-B(7) | 96 (3) |
| O(2)-U(1)-B(4) | 87 (2) | B(6)-U(2)-B(8) | 93 (4) |
| B(1)-U(1)-B(2) | 176 (4) | B(7)-U(2)-B(8) | 108 (4) |
| B(1)-U(1)-B(3) | 81 (3) | C(1)-O(1)-C(4) | 112 (8) |
| B(1)-U(1)-B(4) | 84 (3) | C(7)-O(2)-C(10) | 116 (6) |
| B(2)-U(1)-B(3) | 103 (4) | C(1)-C(2)-C(3) | 106 (5) |
| B(2)-U(1)-B(4) | 92 (4) | C(4)-C(5)-C(6) | 114 (8) |
| B(3)-U(1)-B(4) | 165 (3) | C(7)-C(8)-C(9) | 102 (5) |
| | | C(10)-C(11)-C(12) | 111 (6) |

**Figure 1.** ORTEP view of the U(BH₄)₄·O(*n*-C₃H₇)₂ dimer.

ether ligands at the apices and four borohydride groups about the equator; the second uranium atom is associated with five borohydride groups alone. The first uranium atom environment is reminiscent of that found in the U(BH₄)₄·2THF structure⁴ but lacks one hydrogen atom neighbor.

The nearest neighbors of uranium are the two oxygen atoms and the hydrogen atoms from the borohydride ions. The bridging borohydride contributes two hydrogen neighbors, whereas the terminal ones each contribute three. The interatomic U-B distances of 2.9 and 2.5 Å are characteristic of the two types observed in U(BH₄)₄.¹¹ The first uranium atom has 13 nearest neighbors, including the oxygen atoms, and the second uranium atom has 14 neighbors, all hydrogen atoms. Fourteen-coordination for uranium has been found in U(BH₄)₄,¹¹ U(BH₄)₄·O(CH₃)₂,³ U(BH₄)₄·O(C₂H₅)₂,³ and U(BH₄)₄·2OC₄H₈,⁴ but the thirteen-coordination is unique.

The positions found for the oxygen atoms and for boron atoms 3-8 in the unrestrained refinement are not significantly different from those reported in our final structure, and the distances of these atoms from uranium are the same as listed in Table II within 0.00-0.08 Å. On the other hand, carbon-carbon bonds ranged from 1.36 to 1.73 Å and carbon-oxygen bonds from 1.50 to 2.00 Å, B(2) was 2.04 Å from U(1), and B(1) was 3.13 Å from U(1) and 2.62 Å from U(2). This distance for B(2) is too short for any type of bonding appropriate for this substance and is closer to that for triple-hydrogen bridging than to any other alternative. One may argue that B(1) is triply bridged to U(2) and singly bridged to U(1), but we reject that alternative for the following reasons. The Patterson vectors U(1)-B(1), B(2)-U(1), and B(1)-U(2) are nearly coincident, and we suspect that some systematic errors in the data are working to shift both B(1) and B(2) from

the correct positions. Inspection of Fourier maps causes us to doubt the significance of any deviation of B(1) from the midpoint between U(1) and U(2). We would expect a significantly longer U(1)–U(2) distance if B(1) were singly bridged to one and triply bridged to the other. Finally, this model would give an unprecedented coordination number of 15 hydrogen atoms to U(2). Thus, while the diffraction data are not as definite as we would like, we recognize no acceptable alternative for the assignment of hydrogen neighbors.

The poor definition of the carbon atoms we believe reflects real variability of the positions of the propyl groups in the crystal structure.

A discussion of the volatility properties of this material must involve the molecular constitution of the vapor phase, which is not yet established. The discovery of this curious unsymmetrical dimer tends to complicate, rather than simplify, this question.

Registry No. U(BH₄)₄, 38903-76-3; [U(BH₄)₄O(*n*-C₃H₇)₂]₂, 65150-34-7.

Supplementary Material Available: Data processing formulas, a table of thermal parameters, coordinates and bond distances from the unrestrained refinements, and a listing of observed structure factors (12 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) This work was done with support from the U.S. Energy Research and Development Administration.
- (2) R. R. Rietz and N. M. Edelstein, to be submitted for publication.
- (3) R. R. Rietz, A. Zalkin, D. H. Templeton, N. M. Edelstein, and L. K. Templeton, companion paper, this issue.
- (4) R. R. Rietz, N. M. Edelstein, H. Ruben, D. H. Templeton, and A. Zalkin, companion paper, this issue.
- (5) H. I. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.*, **75**, 219 (1953).
- (6) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
- (7) J. Waser, *Acta Crystallogr.*, **16**, 1091 (1963).
- (8) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).
- (9) D. T. Cromer and J. T. Waber, *Acta Crystallogr., Sect. A*, **18**, 104 (1965).
- (10) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
- (11) E. R. Bernstein, W. C. Hamilton, T. A. Keiderling, S. J. La Placa, S. J. Lippard, and J. J. Mayerle, *Inorg. Chem.*, **11**, 3009 (1972).

Contribution from the Laboratoire de Chimie Minérale Moléculaire, Equipe de Recherche Associée au CNRS, Parc de Valrose, 06034 Nice Cedex, France, and the Institut de Cristallographie, Université de Lausanne, BSP, Dorigny, 1015 Lausanne, Switzerland

Structural and Stereodynamic Studies on Molecular Early Transition Metal Derivatives.

4. Synthesis, Crystal Structure, and Molecular Constitution of Solutions of Bis(alkoxo)trichloroniobium(V)–Hexamethylphosphortriamide Adducts

LILIANE HUBERT-PFALZGRAF,*^{1a} ALAN A. PINKERTON,^{1b} and JEAN G. RIESS^{1a}

Received July 27, 1977

Compounds NbCl₃(OR)₂HMPA (R = Me, *i*-Pr; HMPA = OP(NMe₂)₃) were obtained by disproportionation of [NbCl₂(OR)₃]₂ in methylene chloride or ether in the presence of HMPA. The products are characterized by IR, NMR, and mass spectrometry. An x-ray analysis on NbCl₃(O-*i*-Pr)₂HMPA shows that it crystallizes in the monoclinic space group P2₁/n with unit cell dimensions *a* = 8.570 (2) Å, *b* = 14.087 (3) Å, *c* = 19.374 (3) Å, β = 94.80 (1)°, and Z = 4. The structure refined to R = 0.068. The crystal is built up of the meridional isomer; the two alkoxy groups are cis to each other, one of them being trans to the HMPA ligand. The two Nb–O-*i*-Pr bonds have comparable lengths and their shortness (1.81 Å average) implies a considerable d_π–p_π contribution to the implicit bonding. A trans weakening was observed for the Nb–Cl bond trans to an alkoxy group. The same geometrical isomer was always found to be the predominant species in fresh solutions, while oxo species were detected in aged solutions.

Introduction

We wish to report the unexpected isolation of the dialkoxotrichloroniobium adducts NbCl₃(OR)₂OP(NMe₂)₃ (R = Me, *i*-Pr) which resulted from the reaction of trialkoxodichloroniobium [NbCl₂(OR)₃]₂ with hexamethylphosphortriamide (HMPA) in dichloromethane or diethyl ether. Our initial aim was in fact to prepare the niobium oxoalkoxides NbO(OR)₃ or their adducts through an oxygen vs. chlorine exchange reaction between [NbCl₂(OR)₃]₂ and an oxo-type ligand such as dimethyl sulfoxide (Me₂SO) or HMPA. This exchange reaction, which is known to occur with the niobium pentahalides^{2a} and methylniobium tetrahalides,^{2b} was expected to provide a second synthetic route as an alternative to the reaction of NbOCl₃ with the alcohol in the presence of ammonia, which failed to give us the desired niobium oxoalkoxide in the case where R = Me.

Several niobium(V) halide alkoxides have already been isolated, but there is no information available about their structure, the molecular constitution of their solutions, and their coordination properties. Adducts NbCl₄(OR)·MeCN³⁻⁵ (R = Me, Et) and NbCl₃(OMe)₂·MeCN³ had been obtained when the niobium pentachloride and pentaalkoxide were mixed in the appropriate ratio in acetonitrile. Compound NbCl₃(OEt)₂·MeCOOEt was isolated by reacting MeCOCl with

[NbCl₂(OEt)₃]₂ and further afforded NbCl₃(OEt)₂·py by addition of pyridine.⁴ On the other hand, a phosphine adduct, NbCl₃(OEt)₂·PPh₃, was prepared by reacting NbCl₃·PPh₃ with EtOH in CCl₄.⁶

The present paper describes the reaction of [NbCl₂(OR)₃]₂ with HMPA, the isolation and spectral characterization of the redistribution products NbCl₃(OR)₂·HMPA (R = Me, *i*-Pr), an x-ray diffraction structure of the adduct where R = *i*-Pr, and a preliminary picture of the molecular constitution of their solutions.

Experimental Section

All handling of compounds was carried out under dry argon. HMPA (gift from Pierrefitte), Me₂SO, and solvents were purified and dried according to standard methods. Niobium pentachloride was obtained by chlorination of the metal (gift from Produits Chimiques Ugine Kuhlmann). NbCl₂(OMe)₃ was prepared by reaction of an excess of methanol with NbCl₃ in benzene and recrystallized in a mixture of methylene chloride and toluene.

The ¹H NMR spectra were measured on solutions kept in sealed tubes with a JEOL C-60 HL spectrometer equipped with a variable-temperature system. Me₄Si was used as an internal reference. The infrared spectra were recorded on Nujol mulls on a Perkin-Elmer 577 spectrometer. The conductance measurements were performed with a Taccussel CDN6 conductometer. The molecular weight data were obtained on a Knauer vapor pressure osmometer. The mass