of the coupling of the cyanamide group with the phenyl ring and the perturbation introduced by the nature of the phenyl ring substituents. It is to be expected that electron-withdrawing substituents will stabilize the anion ligand whereas electron-donating substituents will have the opposite effect.

In conclusion, the interaction of Cu(II) with phenylcyanamide anion ligands has been investigated. Crystal structure data, LMCT band intensity, and electrochemical potentials are consistent with a mostly σ bonding interaction between Cu(II) and the cyanamide anion group. Nevertheless, some π interaction must occur for the $p\pi \rightarrow d_{x^2-y^2}$ transition to be partially allowed. This is relevant to the mechanism by which the mixed-valence state of copper in Cu(DCNQI)$_2$ molecular metals is achieved. In future studies, we hope to more accurately model the coordination environment of copper in Cu(DCNQI)$_2$ molecular metals by preparing tetrahedral copper(I) and -(II) complexes of radical anion DCNQI molecules.

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Supplementary Material Available: Tables listing crystal data, atomic positional parameters, bond lengths, bond angles, anisotropic thermal parameters for non-hydrogen atoms, and least-squares planes and deviations therefrom for **1** and **2** (16 pages); structure factor tables for **1** and **2** (55 pages). Ordering information is given on any current masthead page.

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A Homoleptic Uranium Thiolate: Synthesis, Structure, and Fluxional Behavior of [Li(dme)]$_4$[U(SCH$_2$CH$_2$S)$_4$] and Reaction with CS$_2$

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We have synthesized and fully characterized a tetrakis(ethane-1,2-dithiolato)uranate(IV), [Li(dme)]$_4$[U(edt)$_4$] (**1**), the first homoleptic dithiolate complex of an f element. The complex crystallizes with an additional DME solvent molecule, and its structure was determined by an X-ray study. The coordination geometry about the uranium center is dodecahedral, and four lithium cations surround the [U(edt)$_4$]$^{4-}$ anion. Each lithium bridges two sulfur atoms and is further coordinated by a dme molecule. We have analyzed the nature of the U-S bonds, using the enxtended Hückel method, to find that U 6d, 7s, and 7p orbitals are responsible for interactions with sulfur orbitals, thus, no significant U 5f participation in bonding is discernible, and that U-S π interactions are weak. The low-temperature ^{1}H NMR spectra in THF-d_8 exhibit four resonances associated with the edt protons. The relative size of their paramagnetic isotropic shifts can be interpreted on the basis of the pseudocontact (dipolar) term, the analysis of which suggests the solid-state dodecahedral structure to be retained in solution. According to the temperature dependence of the edt proton resonances, there are two fluxional processes, (1) a conformational change of the $\overline{\mathrm{USCCS}}$ chelate rings and (2) an exchange of the A and B sites in the dodecahedral US$_8$ frame. The free energies of activation, $\Delta G^{\ddagger}$, are 9.3-9.6 kcal/mol and 12.9 kcal/mol, respectively, which are rather high probably due to coordination of lithium ions to sulfurs. The complex **1** reacts with CS$_2$ to give [Li(dme)$_2$]$_2$(S$_2$CSCH$_2$CH$_2$SCS$_2$) (**2**) as an isolable product. The crystal structure analysis of **2** reveals a zigzag form of the ethane-1,2-diyl bis(trithiocarbonate) skeleton and η^2 coordination of each trithiocarbonate to a lithium. Crystal data: **1**, solvated by DME, monoclinic space group $P2_1/n$ with a = 11.330 (3) Å, b = 38.454 (8) Å, c = 11.047 (2) Å, β = 95.31 (2)°, Z = 4, R = 0.0538 for 3047 independent reflections; **2**, monoclinic space group $P2_1/n$ with a = 8.827 (3) Å, b = 15.191 (8) Å, c = 13.304 (8) Å, β = 107.13 (4)°, Z = 2, R = 0.0503 for 1581 independent reflections.

Introduction

In contrast to the extensive coordination chemistry of actinide metal ions with oxygen donors,[1] development of their chemistry with S-donor ligands is limited. Some (thiocarbamato)- and (dithiocarbamato)uranyl complexes,[2] (dithiaacetato)uranyl complexes,[2h] a dmso adduct of uranyl,[2i] tetrakis(dithiocarbamato) and tetrakis(dithiophosphinato) complexes of thorium and/or neptunium,[3] a pentasulfido complex of bis(pentamethylcyclopentadienyl)thorium,[4a] a series of binary and ternary uranium sulfides,[4b-e] and an intriguing η^2-disulfide complex of uranyl[2c] have been structurally characterized. Recently the reactions of tris(cyclopentadienyl)uranium(III) with CS$_2$ and SPPh$_3$ (or COS) were reported to form the tetravalent binuclear uranium complexes consisting of CS$_2$ and S atom bridges, respectively.[5] Although synthesis of the pyrophoric U(SEt)$_4$ and U(S^{t}Bu)$_4$ was reported as early as 1956,[6a] actinide thiolate complexes have been virtually ignored,[6b,c] in spite of the fact that thiolates may be useful for the separation of actinide ions from dilute aqueous solution.[6d] This is somewhat surprising in light of the richness of d-transition-metal thiolate chemistry that has been developed partly due to its biological and catalytic implication.

As an outgrowth of our recent studies on alkanedithiolate complexes of group 5 metals,[7a-f] we are interested in the behavior of dithiolate ligands with other electron-deficient metals. Here we report the synthesis, X-ray structure, and variable-temperature ^{1}H NMR study of a tetrakis(ethane-1,2-dithiolato) (edt) complex

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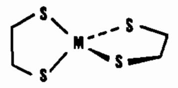
Table I. Crystallographic Data for $[Li(dme)]_4[U(SCH_2CH_2S)_4]$ (**1**) and $[Li(dme)_2]_2[S_2CSCH_2CH_2SCS_2]$ (**2**)

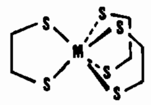
	1	**2**
formula		
molecule	$ULi_4S_8C_{24}H_{56}O_8$	$Li_2C_{20}H_{44}O_8S_6$
solvent	$C_4H_{10}O_2$	
fw	1085.1	618.8
space group	$P2_1/n$	$P2_1/n$
a, Å	11.330 (3)	8.827 (3)
b, Å	38.454 (8)	15.191 (8)
c, Å	11.047 (2)	13.304 (8)
β, deg	95.31 (2)	107.13 (4)
V, Å^3	4792 (2)	1705 (1)
ρ_{calcd}, g cm^{-3}	1.50	1.21
Z	4	2
μ, cm^{-1}	35.9	4.18
radiation	Mo Kα	Mo Kα
final R value	0.0541	0.0503
	$R_G = 0.0612$	$R_w = 0.0630$

of uranium(IV), $[Li(dme)]_4[U(SCH_2CH_2S)_4]$ (**1**), which is the first well-characterized homoleptic dithiolato complex of any lanthanide or actinide ion.[8,9] Dithiolate ligands form d-metal complexes having square-planar (A), tetrahedral (B),[10] and octahedral–trigonal prismatic (C)[7c,11] geometries. The dodecahedral structure (D) of **1** adds another example to the structural diversity.

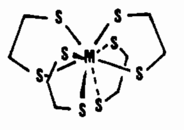
A



B



C



D

We have also analyzed bonding properties of **1** by molecular orbital calculations in the quasi-relativistic extended Hückel framework. In addition, the formation and X-ray structure of $[Li(dme)]_2[S_2CSCH_2CH_2SCS_2]$ (**2**), which results from the reaction of **1** with CS_2, is described in this paper.

Experimental Section

All operations and manipulation were carried out under an argon atmosphere by using standard Schlenk techniques. Reagent grade tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were deoxygenated, dried by reflux over sodium benzophenone, and distilled under argon before use. Carbon disulfide and THF-d_8 were purified by trap-to-trap distillation from calcium hydride and sodium, respectively. Li_2edt was obtained as a white precipitate after the reaction of stoichiometric amounts of butyllithium and H_2edt in hexane. ^1H NMR spectra were recorded on a JEOL FX-90 and JEOL GSX-400 spectrometers, and the data are listed in ppm downfield from TMS. UV-visible spectra were obtained on JASCO UNIDEV-500 and JASCO U-best-30 spectrometers, while IR spectra were measured on a JASCO DS-402G spectrometer.

Preparation of $[Li(dme)]_4[U(SCH_2CH_2S)_4]$·DME (1). A DME slurry (20 mL) of UCl_4 (0.50 g, 1.3 mmol) was carefully added to a DME suspension (15 mL) of Li_2edt (0.42 g, 4.0 mmol) under an argon atmosphere. The mixture was stirred for 1.5 h at 0 °C. After insoluble materials were filtered off through a medium-porosity glass frit, the bright yellow-green solution was concentrated to ca. one-fifth of its original volume. It was then cooled to −20 °C for one night, during which $[Li(dme)]_4[U(SCH_2CH_2S)_4]$·DME (**1**) crystallized as apple green prisms (0.47 g, 43% yield based on Li_2edt). **1** can also be synthesized from a 1:4 mixture of UCl_4 and Li_2edt in THF, followed by recrystallization from DME (ca. 20% yield), mp 150 °C dec. ^1H NMR (THF-d_8, 100 MHz): data are given in the text and in Figure 3. UV-visible (λ_{max}, nm (ϵ, M^{-1} cm^{-1}); THF): 731 (80), 704 (230), 696 (150), 663 (150), 635 (60), 595 (70), 537 (110), 509 (110), 461 (160).

X-ray Crystallographic Study of 1. A crystal of $[Li(dme)]_4[U(SCH_2CH_2S)_4]$·DME from the preparation described above was selected and sealed in a thin-walled glass capillary under argon. A Syntex P$\bar{1}$ diffractometer operating at ambient temperature was used to collect the diffraction data, with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The unit cell constants were determined by least-squares refinements of the orientation angles of 15 centered reflections in the range 22° < 2θ < 39°. The crystal was found to contain one very long

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axis (38.45 Å). This was confirmed by recalculating the axial length on the basis of an axial photograph. The reflection data were then collected by the ω-scan technique, where three check reflections were periodically recorded to monitor the stability and orientation of the crystals. They showed no systematic decay throughout the data collection. Details of crystal data and other relevant information are summarized in Table I. The intensity measurements were corrected for Lorentz and polarization effects and for absorption, by using the program PROCESS[12] and measured ψ scans for four reflections.

The structure was solved by the standard heavy-atom method with the SHELX-76 package,[13] in space group $P2_1/n$ that was suggested by systematic absences. The position of the uranium atom determined from the Patterson projection was confirmed by a direct-methods solution obtained from the MULTAN 80 program. The remaining non-hydrogen atoms were located in a series of Fourier maps and full-matrix least-squares refinements. Atomic scattering factors for S, O, C, and H were supplied by SHELX-76, and those of U and Li were taken from the literature.[14] The refinements were done by using 3047 observed reflections with $|F_o|^2 > 3.0\sigma(|F_o|^2)$ out of the 4067 unique reflections. The uranium and sulfur atoms were refined anisotropically, while the other non-hydrogen atoms were refined isotropically, to give the R value of 0.0715 when absorption corrections were not applied. At this stage, four well-behaved DME's and the U(edt)$_4$ portion merged into a single complex molecule with four lithium atoms bridging them. Refining the fifth DME molecule showed each atom of the crystal solvent to be fully occupied, but their thermal parameters were high.

Introduction of absorption corrections lowered the R value to 0.0583. Then hydrogen positions were calculated, where the methylene protons were constrained to ride on the carbons to which they are bonded and the methyl groups were treated as rigid groups. Refinement converged at R = 0.0541, and a final difference Fourier map showed the maximum peak of 0.78 e/Å^3 in the vicinity of the U atom. The atomic positional parameters of all non-hydrogen atoms are listed in Table II along with the equivalent isotropic thermal parameters U_{eq}. Additional crystallographic data are available as supplementary material that includes tables of anisotropic temperature factors, atomic parameters for hydrogen atoms and the solvent DME molecules, and observed and calculated structure factors.

Reaction of [Li(dme)]$_4$[U(SCH$_2$CH$_2$S)$_4$] with CS$_2$. An excess amount of carbon disulfide (0.4 mL, 7 mmol) was added at 0 °C to a solution of [Li(dme)]$_4$[U(SCH$_2$CH$_2$S)$_4$]·DME (0.14 g, 0.13 mmol) in 10 mL of DME. A yellow brown precipitate formed immediately, and the color of the solution changed from pale green to yellow. The reaction mixture was then warmed to room temperature and was stirred for 2 h. After separation of the precipitate, the solution was concentrated to about 2 mL and was kept at −20 °C overnight. During this time, yellow needles of [Li(dme)$_2$]$_2$[S$_2$CSCH$_2$CH$_2$SCS$_2$] (**2**) (0.05 g, 0.09 mmol) were formed (33% yield based on Li), mp 88–92 °C. ^{1}H NMR (D$_2$O, 400 MHz; δ, ppm): 3.26 (s, 24 H, CH_3OCH$_2$CH$_2$OCH_3), 3.40 (s, 4 H, S$_2$CSCH_2CH_2SCS$_2$), 3.49 (s, 16 H, CH$_3$OCH_2CH_2OCH$_3$). UV–visible (λ_{max}, nm; THF): 334, 300. IR (KBr; ν_{max}, cm^{-1}): 1140 (m), 1380 (m), 1360 (m), 1270 (w), 1238 (m), 1190 (m), 1158 (w), 1115 (s), 1065 (s), 985 (s), 825 (s), 710 (m).

X-ray Crystallographic Study of 2. A crystal of **2** from the reaction described above was mounted in a thin-walled glass capillary under argon. A Nicolet R3m/V-200 crystallographic system with a Nicolet P3 diffractometer was used for data collection, structure solution, and refinement. Cell constants were determined by least-squares methods from the centered angular coordinates of 23 intense reflections. The intensity measurements were corrected for Lorentz and polarization effects and for absorption. Systematic absences indicated the space group $P2_1/n$. The coordinates of three of the sulfur atoms were obtained in an initial direct-methods solution, and the remaining atoms were located in difference maps during subsequent cycles of full-matrix least-squares refinement using 1581 reflections with $|F_o|^2 > \sigma(|F_o|^2)$. SCH$_2CH_2$S, which joints the two [(dme)$_2$Li(S$_2$C–)] units, is disordered over two conformations; the occupancies of the atoms of the major conformation, S(3) and C(10), refined to 0.66 (3), and the occupancies refined to 0.34 (3) for the atoms of the minor conformation. During final cycles of least squares, all non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed at calculated positions with the parameters contained in SHELXTL. Final R values are R = 0.0503 and R_w = 0.0630. Tables of anisotropic temperature factors, hydrogen atom parameters, and observed and calculated structure factors are given in the supplementary material.

Table II. Atomic Coordinates of Non-Hydrogen Atoms in **1** and **2** with Esd's in Parentheses

atom	x	y	z	U_{eq}[a]
		(a) [Li(dme)]$_4$[U(SCH$_2$CH$_2$S)$_4$] (**1**)		
U	0.8317 (1)	0.1293 (0)	0.1546 (1)	0.043
S(1)	1.0511 (5)	0.0971 (1)	0.1126 (5)	0.066
S(2)	1.0092 (5)	0.1821 (1)	0.1264 (5)	0.058
S(3)	0.7687 (5)	0.1373 (1)	−0.0951 (4)	0.064
S(4)	0.7744 (5)	0.0616 (1)	0.0519 (5)	0.063
S(5)	0.5985 (4)	0.1302 (2)	0.2161 (4)	0.064
S(6)	0.7430 (5)	0.1984 (1)	0.1194 (5)	0.067
S(7)	0.9176 (5)	0.1504 (1)	0.3907 (4)	0.059
S(8)	0.8042 (5)	0.0723 (1)	0.3215 (5)	0.061
C(1)	1.163 (2)	0.1263 (5)	0.192 (2)	0.075
C(2)	1.150 (2)	0.1613 (5)	0.140 (2)	0.073
C(3)	0.808 (2)	0.0965 (5)	−0.161 (2)	0.076
C(4)	0.744 (2)	0.0662 (5)	−0.113 (2)	0.068
C(5)	0.583 (2)	0.1988 (6)	0.136 (2)	0.094
C(6)	0.532 (2)	0.1633 (5)	0.117 (2)	0.061
C(7)	0.824 (2)	0.1269 (5)	0.490 (2)	0.067
C(8)	0.841 (2)	0.0870 (5)	0.477 (2)	0.078
C(11)	0.924 (2)	−0.0214 (7)	0.129 (2)	0.127
C(12)	1.039 (2)	−0.0173 (7)	0.316 (2)	0.110
C(13)	1.135 (2)	0.0038 (6)	0.379 (2)	0.098
C(14)	1.182 (3)	0.0630 (7)	0.442 (3)	0.131
C(21)	1.017 (3)	0.2687 (8)	0.290 (3)	0.140
C(22)	0.832 (2)	0.2771 (6)	0.379 (2)	0.093
C(23)	0.757 (2)	0.2631 (6)	0.463 (2)	0.094
C(24)	0.653 (2)	0.2107 (7)	0.492 (2)	0.123
C(31)	0.399 (3)	0.0847 (8)	−0.035 (3)	0.151
C(32)	0.372 (3)	0.0369 (8)	0.106 (3)	0.137
C(33)	0.435 (3)	0.0119 (9)	0.169 (3)	0.161
C(34)	0.599 (4)	0.001 (1)	0.301 (4)	0.227
C(41)	0.873 (2)	0.2352 (7)	−0.172 (2)	0.124
C(42)	0.981 (3)	0.2019 (8)	−0.303 (3)	0.141
C(43)	1.068 (2)	0.1758 (7)	−0.308 (2)	0.115
C(44)	1.127 (3)	0.1230 (9)	−0.219 (3)	0.191
O(11)	1.004 (1)	−0.0005 (4)	0.205 (1)	0.085
O(12)	1.092 (1)	0.0389 (4)	0.392 (1)	0.092
O(21)	0.929 (1)	0.2541 (4)	0.360 (1)	0.089
O(22)	0.725 (1)	0.2292 (4)	0.419 (2)	0.098
O(31)	0.451 (2)	0.0589 (5)	0.041 (2)	0.110
O(32)	0.529 (2)	0.0261 (5)	0.243 (2)	0.128
O(41)	0.954 (2)	0.2109 (6)	−0.191 (2)	0.143
O(42)	1.056 (2)	0.1514 (5)	−0.212 (2)	0.129
Li(1)	0.979 (3)	0.051 (1)	0.234 (3)	0.079
Li(2)	0.847 (3)	0.2072 (9)	0.323 (3)	0.066
Li(3)	0.602 (4)	0.071 (1)	0.157 (4)	0.090
Li(4)	0.959 (4)	0.168 (1)	−0.084 (4)	0.099
		(b) [Li(dme)$_2$]$_2$[S$_2$CSCH$_2$CH$_2$SCS$_2$] (**2**)		
Li	0.1679 (7)	0.2831 (4)	0.2014 (4)	0.056
S(1)	0.1793 (1)	0.4162 (1)	0.3378 (1)	0.075
S(2)	−0.1131 (1)	0.3796 (1)	0.1612 (1)	0.086
S(3)	−0.1448 (6)	0.478 (1)	0.3353 (5)	0.086
S	−0.1544 (7)	0.424 (2)	0.357 (1)	0.072
O(1)	0.2837 (3)	0.3580 (2)	0.1047 (2)	0.076
O(2)	0.4081 (3)	0.2398 (2)	0.2566 (2)	0.079
O(3)	0.0851 (4)	0.1852 (2)	0.2989 (3)	0.096
O(4)	0.0710 (4)	0.1830 (2)	0.0976 (2)	0.088
C(1)	−0.0165 (5)	0.4180 (2)	0.2807 (3)	0.063
C(2)	0.4465 (6)	0.3639 (3)	0.1622 (4)	0.082
C(3)	0.5039 (6)	0.2753 (3)	0.1969 (4)	0.092
C(4)	0.2231 (7)	0.4405 (3)	0.0605 (4)	0.106
C(5)	0.4559 (7)	0.1555 (3)	0.2983 (5)	0.117
C(6)	−0.0017 (7)	0.1157 (4)	0.1355 (5)	0.105
C(7)	−0.0356 (8)	0.1369 (4)	0.2313 (5)	0.122
C(8)	0.0928 (7)	0.1678 (4)	0.0009 (4)	0.115
C(9)	0.064 (1)	0.1980 (4)	0.3995 (4)	0.142
C(10)	−0.019 (3)	0.459 (1)	0.508 (2)	0.103
C(11)	−0.035 (3)	0.528 (2)	0.442 (2)	0.071

[a] Defined as one-third of the trace of the orthogonalized U_{ij} tensor in Å^2 unit.

Molecular Orbital Calculations. Quasi-relativistic extended Hückel molecular orbital calculations using the modified Wolfsberg–Helmholz formula[15] were carried out. The basis functions of uranium are of qua-

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(12) Bruck, M. A. PROCESS program. Modified by Carrie, M. J. J., Department of Chemistry, University of Hawaii, 1984.

(13) Sheldrick, G. M. SHELX-76: Program for Crystal Structure Determination. University of Cambridge, England, 1976.

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Table III. Atomic Parameters Used for Extended Hückel Calculations

atom	orbital	H_{ii}, eV	exponent[a]
U	7s	-5.50	1.914
	7p	-5.50	1.914
	6d	-6.67	2.581 (0.7608) + 1.207 (0.4126)
	5f	-7.87	4.943 (0.7844) + 2.106 (0.3908)
	6p	-30.03	4.033
S	3s	-20.00	1.817
	3p	-13.30	1.817
O	2s	-32.30	2.275
	2p	-14.8	2.275
C	2s	-21.40	1.625
	2p	-11.40	1.625
Li	2s	-5.40	0.650
	2p	-3.50	0.650
H	1s	-13.60	1.300

[a] The numbers in parentheses are contraction coefficients used in the double-ζ expansion.

si-relativistic quality. Single-ζ Slater type functions were employed for U 7s, 7p, and 6p orbitals, and double-ζ functions for 6d and 5f orbitals, with the orbital exponents taken from our earlier work.[1h,16] The orbital exponents of S, O, C, Li, and H are the standard ones. The valence-state ionization potentials, H_{ii}, of U 6d and 5f were determined by charge-iterative calculations on $[U(SCH_2CH_2S)_4]^{4-}$, by assuming a quadratic charge dependence of H_{ii} and using the *A*, *B*, and *C* parameters estimated from the Dirac-Slater atomic orbital energies.[16b] During these charge-iterative calculations, the U 7s, 7p, and 6p orbital energies, as well as the standard orbital energies for the other elements, were fixed. Table III summarizes these atomic orbital parameters.

The uranium to sulfur distances were fixed at 2.85 Å as was the S-U-S chelate bite angle at 71°. The two S_4 trapezoids in the dodecahedral US_8 coordination geometry were idealized to be perpendicular, and in each trapezoidal plane the S(A)-U-S(A) and the S(B)-U-S(B) angles were fixed at the values observed in the structure of **1**, 63 and 155°, respectively. For the $SCH_2CH_2S^{2-}$ ligand, all the S-C, C-C, and C-H distances were set at 1.82, 1.50, and 1.09 Å, respectively, while the S-C-C and H-C-H angles were idealized as 120 and 109.47° (tetrahedral). For the Li-containing model complexes, $Li_4[U(SCH_2CH_2S)_4]$ and $[Li(OH_2)_2]_4[U(SCH_2CH_2S)_4]$, the assumed geometrical parameters include the following: Li-S, 2.42 Å; Li-O, 2.06 Å; O-H, 1.0 Å; O-Li-O, tetrahedral; Li-O-H, 120°; Li-OH_2, planar.

Results and Discussion

Synthesis of 1. In an attempt to prepare a homoleptic (ethanedithiolato)uranium(IV) complex, we initially tried the reaction of UCl_4 with 3 equiv of dilithium ethane-1,2-dithiolate in THF, following our syntheses of the group 5 d^0-metal complexes $[A][M(SCH_2CH_2S)_3]$ ($A = Et_4N$, Ph_4P; M = Nb, Ta).[7c,d] Standard workup and subsequent recrystallization from DME afforded $[Li(dme)]_4[U(SCH_2CH_2S)_4]$ (**1**) as air- and/or moisture-sensitive apple green crystals in ca. 10% yield. With this stoichiometry established, the compound (crystals, 43%) was prepared more rationally in the 1:4 UCl_4-$Li_2S_2C_2H_4$ system in DME. These crystals also contain an uncoordinated DME solvent molecule. Regardless of the reaction ratio and of the choice of solvents, the isolable product is a tetrakis(ethanedithiolato) complex of U(IV).

$$UCl_4 + 4Li_2(SCH_2CH_2S) \xrightarrow[\text{in DME}]{} \underset{\substack{\textbf{1}\\ \text{apple green crystals}\\ \text{yield 43\%}}}{[Li(dme)]_4[U(SCH_2CH_2S)_4]\cdot DME}$$

The UV-visible spectrum of **1** exhibits weak but relatively narrow peaks in the 420-740-nm range. The low extinction coefficients (ϵ) of 80-230 indicate that these peaks arise from forbidden f-f transitions of the f^2 U(IV) center. In contrast, $[Nb(edt)_3]^-$ and $[Ta(edt)_3]^-$ have three intense bands assignable to sulfur(p)-to-metal(d) transitions at 325, 386, and 523 nm for the Nb complex and at 291, 332, and 442 nm for the Ta complex.[7c,d] Provided that the analogous ligand-to-metal charge-transfer transitions should occur for **1**, they would be a sulfur (p)-to-uranium (6d) type. The absence of intense bands in the measured region is consistent with the idea that uranium 6d levels are higher in energy than 4d levels of Nb and 5d levels of Ta[17] and thereby such a charge-transfer transition would be largely blue-shifted.

Solid-State Structure of 1. The molecular structure of **1** was determined by a single-crystal X-ray diffraction analysis. An

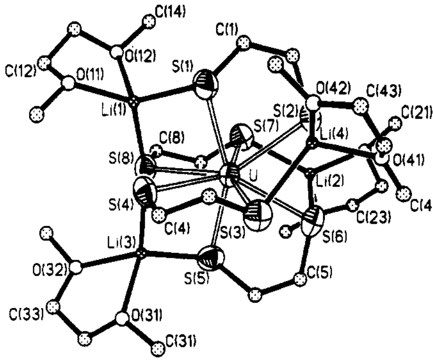

Figure 1. ORTEP view of the entire molecule of $[Li(dme)]_4[U(edt)_4]$ (**1**), showing the atom-labeling scheme used in the tables. Hydrogen atom positions are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for $[Li(dme)]_4[U(SCH_2CH_2S)_4]$ (**1**) with Esd's in Parentheses

U-S(1)	2.854 (4)	U-S(2)	2.895 (4)
U-S(3)	2.801 (4)	U-S(4)	2.889 (4)
U-S(5)	2.789 (4)	U-S(6)	2.855 (4)
U-S(7)	2.818 (4)	U-S(8)	2.900 (4)
av U-S(B site)	2.816	av U-S(A site)	2.885
S(1)-C(1)	1.85 (2)	S(2)-C(2)	1.78 (2)
S(3)-C(3)	1.81 (2)	S(4)-C(4)	1.83 (2)
S(5)-C(6)	1.79 (2)	S(6)-C(5)	1.84 (2)
S(7)-C(7)	1.83 (2)	S(8)-C(8)	1.82 (2)
C(1)-C(2)	1.47 (2)	C(3)-C(4)	1.50 (2)
C(5)-C(6)	1.49 (3)	C(7)-C(8)	1.56 (3)
Li(1)-S(1)	2.41 (4)	Li(1)-S(8)	2.43 (4)
Li(2)-S(6)	2.46 (4)	Li(2)-S(7)	2.42 (3)
Li(3)-S(4)	2.39 (4)	Li(3)-S(5)	2.36 (4)
Li(4)-S(2)	2.40 (4)	Li(4)-S(3)	2.45 (4)
Li(1)-O(11)	2.02 (4)	Li(1)-O(12)	2.12 (4)
Li(2)-O(21)	2.05 (4)	Li(2)-O(22)	2.01 (4)
Li(3)-O(31)	2.10 (5)	Li(3)-O(32)	2.17 (5)
Li(4)-O(41)	2.02 (5)	Li(4)-O(42)	1.97 (5)
S(1)-U-S(2)	70.3 (1)	S(1)-U-S(4)	73.3 (1)
S(1)-U-S(5)	154.8 (1)	S(1)-U-S(8)	85.5 (1)
S(2)-U-S(3)	86.2 (1)	S(2)-U-S(6)	64.6 (1)
S(2)-U-S(7)	73.4 (1)	S(3)-U-S(4)	71.6 (1)
S(3)-U-S(6)	73.1 (1)	S(3)-U-S(7)	156.1 (1)
S(4)-U-S(5)	85.6 (1)	S(4)-U-S(8)	62.3 (1)
S(6)-U-S(7)	86.9 (1)	S(7)-U-S(8)	71.0 (1)
U-S(1)-C(1)	103.3 (6)	U-S(2)-C(2)	107.6 (6)
U-S(3)-C(3)	104.6 (6)	U-S(4)-C(4)	108.6 (6)
U-S(5)-C(6)	102.3 (6)	U-S(6)-C(5)	109.3 (8)
U-S(7)-C(7)	104.0 (6)	U-S(8)-C(8)	109.7 (6)
S(1)-C(1)-C(2)	110 (1)	S(2)-C(2)-C(1)	120 (1)
S(3)-C(3)-C(4)	113 (1)	S(4)-C(4)-C(3)	112 (1)
S(5)-C(6)-C(5)	115 (1)	S(6)-C(5)-C(6)	111 (2)
S(7)-C(7)-C(8)	111 (1)	S(8)-C(8)-C(7)	112 (1)
S(1)-Li(1)-S(8)	107 (1)	S(6)-Li(2)-S(7)	106 (1)
S(4)-Li(3)-S(5)	108 (2)	S(2)-Li(4)-S(3)	107 (2)
O(11)-Li(1)-O(12)	81 (1)	O(21)-Li(2)-O(22)	81 (1)
O(31)-Li(3)-O(32)	76 (2)	O(41)-Li(4)-O(42)	80 (2)

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(17) For example, see: Desclaux, J. P. *At. Data Nucl. Data Tables* **1973**, *12*, 311-406.

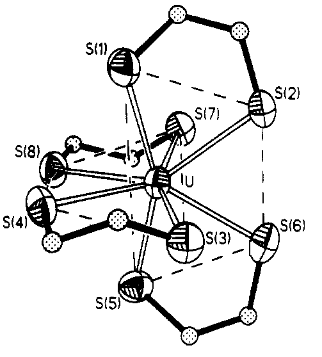


Figure 2. ORTEP view of the $[U(edt)_4]^{4-}$ portion of **1**, drawn at the 50% probability level. Emphasized are the two trapezoidal planes in the dodecahedral coordination geometry.

Table V. Comparison of Shape Parameters between **1** and Three Idealized 8-Coordination Geometries[a,b]

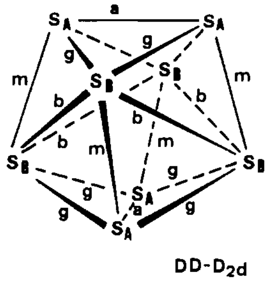
	ϕ^1	ϕ^2	δ'			
DD, D_{2d}	0.0	0.0	29.5	29.5	29.5	29.5
BTP, C_{2v}	14.1	14.1	0.0	21.8	48.2	48.2
SAP, D_{4d}	24.5	24.5	0.0	0.0	52.4	52.4
$[U(edt)_4]^{4-}$	11.7	13.1	36.4	38.0	37.4	35.4

[a] DD, dodecahedron; BTP, bicapped trigonal prism; SAP, square antiprism. [b] The shape parameters for the idealized geometries were taken from ref 19.

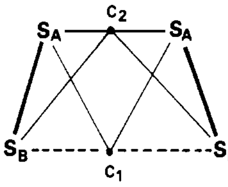
ORTEP drawing of the entire molecule is shown in Figure 1, with the numbering scheme adopted. Selected bond distances angles are listed in Table IV.

At the center of the molecule, uranium is chelated by four ethanedithiolato ligands, each of which occurs with a half-chair conformation. Four lithium cations surround this $[U(edt)_4]^{4-}$ anion in a tetrahedral array with respect to the central uranium, thus neutralizing the molecule. Then each lithium is further coordinated by a dme molecule. Alternatively, the molecule can be viewed as a multilayered onionlike structure: the uranium atom is at its center, the edt ligands occupy the innermost layer, the lithiums form the next layer, and then the outermost layer is defined by four dme molecules.

The geometry of the US_8 frame is dodecahedral (DD), as can be seen in the perspective view of the $[U(edt)_4]^{4-}$ portion (Figure 2), or more specifically it is designated *mmmm*-D_{2d} in terms of its chelate-ligand wrapping pattern and the approximate point group symmetry.[18] The pseudo-2-fold, pseudo-S_4 axis passes through the uranium center and the midpoints of the two opposite *a* edges defined by S(2) and S(6) and by S(4) and S(8). The ideal DD contains two orthogonal trapezoidal planes with ligands occupying their *m* edges. For **1**, two trapezoids can be defined by the S1–S2–S6–S5 and S3–S4–S8–S7 atoms, which are, in fact, nearly perpendicular to each other (90.5°). The maximum deviation from the weighted least-squares trapezoidal planes occurs at S(2) (0.298 Å) and S(6) (−0.274 Å) and at S(4) (0.241 Å) and S(8) (−0.241 Å), respectively. Departure from the ideal dodecahedron (E) may also be measured by shape parameters ϕ^1 and ϕ^2 that are the dihedral angles between two triangles constructed from the trapezoidal atoms, as shown in F, and also by the dihedral angles δ' associated with the shape-determining edges.[19,20] These shape parameters were calculated for **1** and are compared with the ideal values for the three limiting 8-coordinate structures in Table V.



E



ϕ = dihedral angle between AAC_1 and BBC_2

F

The ϕ values of **1** depart somewhat from the DD ideal of 0.0° and are close to those of a bicapped trigonal prism (BTP). This distortion is perhaps a consequence of the half-chair-type twist of the edt ligands in the US_2C_2 rings. However, the four nearly equal δ' parameters are actually not far from the ideal value of 29.5°, which suggests the US_8 geometry is best described as a "distorted" DD.

The S–U–S chelate angles are decidedly smaller than the corresponding edt bite angles in d-transition-metal complexes, e.g., $[Et_4N]_2[Ti(edt)_3]$ (82.8–82.9°),[10b,c] $[Ph_4P][VS(edt)_2]$ (84.41°),[21] $[Et_4N][Cr(edt)_2]$ (88.4°),[10b,c] $[Me_4N]_2[Mn(edt)_2]$ (91.5°),[10a] $[n\text{-}Bu_4N]_2[Fe(edt)_2]_2$ (89.5°),[11a] $[Co(edt)_2]^{-,2-}$ (91.7, 91.8°),[10b,c] $[Et_4N][Nb(edt)_3]$ (81.9°),[7c] $(Ph_4P)[MoO(edt)_2]$ (88.6°),[22] and $[Me_4N][ReS(edt)_2]$ (84.9°).[23] Since the S--S bite distances of edt (3.309 (6)–3.331 (6) Å) are not aberrant, we attribute the acute S–U–S bite angles simply to the long U–S bond distances.

The U–S bond lengths fall in the range of known U–S distances of 8-coordinate uraniums:[24a] $[Me_4N][UO_2(R_2NCS_2)_3]$, 2.80 Å (average);[2d] MUS_3 (M = V, Cr, Co, Ni), 2.85 Å;[4b] U_3S_5, 2.939 Å;[4d] CrU_8S_{17}, 2.83 Å (BTP), 2.84 and 2.78 Å (DD);[4b] $[R_2NH_2]_2[UO_2(R_2NCOS)_2(S_2)]$, 2.711 ($S_2$) and 2.873 Å ($R_2NCOS$).[2c] They are also close to the sum of the ionic radius of 8-coordinate U(IV), 1.00 Å, and that of S^{2-}, 1.84 Å.[24b] In the case of $(Cp_3U)_2S$, the presence of U–S π interactions was invoked to explain the very short observed U–S distance of 2.60 Å. Obviously there is no sign of such strong U–S interactions for **1**.

Befitting a DD structure, in which there are two symmetrically unrelated sites conveniently labeled A and B, the U–S bond distances of **1** can be grouped into four long and four short distances, as shown in Table IV. The observed trend of r(U–S(A)) > r(U–S(B)) is also consistent with the theoretical prediction for DD structures of d^0 transition-metal complexes with eight equivalent monodentate ligands, in that atoms at the B site tend to form stronger, and thus shorter, bonds with the central metal; i.e., r(M–A)/r(M–B) > 1.[25] The difference between r(U–S(A)) and r(U–S(B)) is 0.07 Å and is similar to those between r(M–A) and r(M–A) in $Na_4Zr(C_2O_4)_4$ (0.06 Å),[26] $Ti(S_2CNEt_2)_4$ (0.08 Å),[27] $[Ta(S_2CNMe_2)_4][TaCl_6]$ (0.07 Å),[28] and $Ti(SOCNEt_2)_4$

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(24) The U–S distances are similar to the Th–S distances in $Th(S_2CNEt_2)_4$ (average 2.87 Å) and $Th(S_2PR_2)_4$ (average 2.904, 2.911 Å) and to the Np–S distances in $[Et_4N][Np(S_2CNEt_2)_4]$ (average 2.89 Å). See ref 3.

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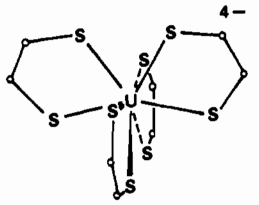
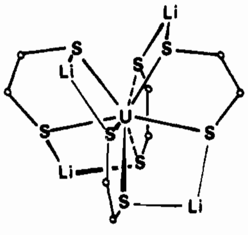
(0.08 (S), 0.06 Å (O))[29] but is larger than those in $Zr(SOCNEt_2)_4$ (0.02 (S), 0.02 Å (O))[29] and $Ti(NO_3)_4$ (0.02 Å).[30]

On the outside of the $[U(edt)_4]^{4-}$ core, there are four lithium ions, each bridging an A- and a B-site sulfur, which belong to different edt ligands. There, four Li ions combined with the four edt ligands may be considered to form a 20-membered macrocycle surrounding the uranium ion. Each lithium is further coordinated by a dme molecule, completing a pseudotetrahedral LiS_2O_2 unit geometry. The average Li–S distance of 2.42 Å is not unusual but is perhaps placed at the short end of the known Li–S distances, 2.516 Å in the dimeric structure of 2-lithio-2-methyl-1,3-dithiane–tmeda,[31] 2.4_2 Å in polymeric CH_3SLi,[32] and 2.44 (2)–2.54 (2) Å in $[Li(thf)]_4[(C_5Me_5)Ta(S)_3]_2$.[33] The Li–O bond distances, which average 2.06 Å, are normal.[34]

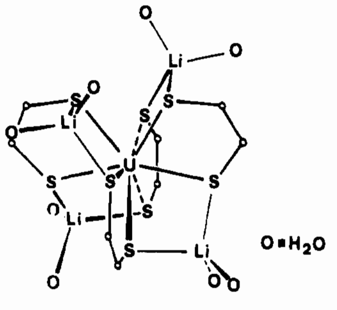
Nature of the U–S Bonds. In order to gain insight into the bonding in **1** and to ascertain if the early theoretical analysis based on the d-metal dodecahedral structures with eight equivalent monodentate ligands can be applied to our edt complex of uranium, we performed extended Hückel calculations on the following three model complexes: the bare anion, $[U(edt)_4]^{4-}$ (G), the Li-containing model, $Li_4[U(edt)_4]$ (H), and finally a model in which two water molecules coordinate at each Li atom in place of dme, $[Li(OH_2)_2]_4[U(edt)_4]$ (I). The USCCS rings were assumed to be planar or were twisted at the CH_2CH_2 portion by 20° to mimic the observed conformation. Other geometrical parameters employed for calculations are detailed in the Experimental Section.



G



H



I

Table VI. Overlap Populations (*P*)[a] and Atomic Charges (*Q*) Calculated for $[U(edt)_4]^{4-}$ (G), $Li_4[U(edt)_4]$ (H), and $[Li(OH_2)_2]_4[U(edt)_4]$ (I)

	G[b]	H[b]	I[b]
$P(U-S(A))$	0.4895	0.5191	0.5197
$P(U-S(A))_\pi$	0.0431	0.0351	0.0355
$P(U_d-S(A))$	0.2450	0.2333	0.2336
$P(U_f-S(A))$	0.0372	0.0358	0.0358
$P(U-S(B))$	0.5663	0.5720	0.5732
$P(U-S(B))_\pi$	0.0731	0.0676	0.0689
$P(U_d-S(B))$	0.2530	0.2399	0.2407
$P(U_f-S(B))$	0.0367	0.0344	0.0349
$P(S(A)\text{--}S(A))$[c]	−0.0784	−0.0720	−0.0713
$P(S\text{--}S)_{all}$	−0.3928	−0.3680	−0.3666
$P(Li-S(A))$		0.2272	0.2181
$P(Li-S(B))$		0.2902	0.2727
$Q(U)$	+0.847	+0.812	+0.808
$Q(S(A))$	−0.700	−0.561	−0.572
$Q(S(B))$	−0.674	−0.489	−0.504
$Q(Li)$		+0.726	+0.683

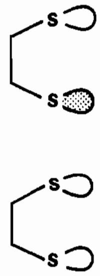
[a] S(A) and S(B) denote sulfur atoms at the A and B sites of the DD structure. $P(U-S(A))_\pi$, etc., represent π components of the U–S overlap populations; $P(U_d-S(A))$, etc., represent contributions from uranium 6d orbitals; $P(S\text{--}S)_{all}$ represents the sum of all S--S nonbonded interactions. [b] Edt ligands are planar, and see text. [c] Overlap population between neighboring A-site sulfur atoms. Note that there are two such interactions in the molecule.

The analysis consists of an inspection of overlap populations (*P*) of U–S and Li–S bonds as well as those for S--S nonbonding interactions. If we move from the planar edt conformation to the twist edt conformation, the calculated energies drop, ipso facto, by 0.74, 0.83, and 0.51 eV for G–I, respectively. However, this conformational change hardly affects the overlap populations under consideration, so that we will concentrate on the analysis of those derived from the planar edt model complexes.

The calculated overlap populations are summarized in Table VI. One obvious feature is that *P*(U–S(A)) is smaller than *P*(U–S(B)) for all the model complexes, suggesting weaker U–S(A) bonds. This is in accord with the X-ray-derived structure of **1** and also with the earlier theoretical result for d^0-transition-metal dodecahedrons. It is also evident that the association of the Li ions is not the reason behind the different U–S(A,B) bond strengths. π interactions contribute very slightly to the U–S(A,B) overlap populations, with $P(U-S(A,B))_\pi$ being as small as 0.035–0.073. Thus, very weak U–S π bonding in **1** is indicated by our theoretical analysis. Decomposition of the U–S overlap populations into contributions from individual uranium orbitals shows that about half of *P*(U–S(A,B)) comes from interactions between U 6d and sulfur orbitals, with another half arising from the U 7s,p components. The U 5f participation in the U–S bonds is minute, as can be seen in the small $P(U_f-S(A,B))$ values.

With four edt ligands surrounding the uranium center, **1** is a very congested molecule. As a consequence, the sum of *P*(S--S) is as negative as −0.393 for G, 40% of which comes from repulsive interactions between two adjacent A-site sulfur atoms, with 33% coming from those between A-site and B-site sulfurs belonging to different edt ligands. The presence of Li cations in H and I somewhat reduces the S--S repulsive interactions but not very much. The sulfur atoms of edt carry two distinct types of lone pairs; one is the higher lying π-type lone pair J orthogonal to the MSCCS plane, and the other is the lower lying σ-type lone pair K in the MSCCS plane. In view of their higher energy levels, one would anticipate that the π orbitals, J, to be better donors,[35]

J



K

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(31) Amstutz, R.; Seebach, D.; Seiler, P.; Achweizer, B.; Dunitz, J. D. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 53–54.
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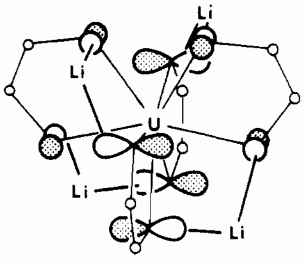
(34) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353–451.

while the σ orbitals, K, have better spatial extension. In **1**, the four Li cations choose positions where they achieve good overlap with the S π-type lone pairs, as shown in L. Interestingly, the addition of four Li^+ ions to bare $[U(edt)_4]^{4-}$ does not weaken the U–S bonds but actually slightly enlarges P(U–S(A,B)).



L

The calculated charges (Q) on the U, S, and Li atoms are also summarized in Table VI. It is understandable that coordination of S to Li, in going from G to H, leads to a reduction of the negative charges on the S atoms and that further coordination of Li by O moves electrons back to sulfur in I. For either G, H, or I, more negative charge accumulates at the A-site sulfurs. This result contrasts with the analysis given for d^0-metal dodecahedrons with eight monodentate ligands where Q(A) was reported to be less negative than Q(B).

Variable-Temperature ^{1}H NMR Study. The solid-state structure of **1** raises the question of whether the DD US_8 geometry is rigid in solution. Examples of solution structures established for 8-coordinate tetrakis chelates are rather limited. The low-temperature ^{1}H NMR spectra of $[Ta(S_2CNMe_2)_4]^+$, $[M(SOCNMe_2)_4]^+$ (M = Nb, Ta), $M(SOCNR_2)_4$ (M = Ti, Zr),[36] WQ_4, and WP_4 (Q = 5,7-dichloro-8-quinolinolate; P = 5-methylpicolinate)[37] were all reported to be compatible with the DD *mmmm* geometries found for their crystal structures, when stereoisomers induced by the unsymmetric nature of the S–O and N–O chelates are left out of consideration. On the other hand, the detailed analysis of the isotropic paramagnetic shifts in the spectra of $U(acac)_4$ has implied a BTP with the ligand wrapping pattern of $h_1h_1p_2p_2$-C_2,[38] which closely resembles the solid-state structure of the β-$U(acac)_4$.[39]

We have measured the variable-temperature 90-MHz ^{1}H NMR spectrum of **1** in THF-d_8 from −70 to +65 °C. In this temperature range, two singlets (approximately 6:4 in ratio) at δ = 3.6 and 3.4 ppm (20 °C) remain sharp and do not display notable isotropic shifts. We assign these to diamagnetic proton resonances arising from free dme molecules. Thus, the dme ligands on Li in **1** apparently are replaced by solvent in THF-d_8, although there remains a slim possibility that dme molecules are still bound to the Li ion in solution and yet are not affected by the paramagnetic uranium center.

In addition to the very sharp dme resonances, we observe in the 65 °C spectrum a relatively broad singlet centered at 18.7 ppm (the width at half-height $\nu_{1/2}$ = 107.2 Hz) attributable to the edt protons. This resonance was found to exhibit an intriguing temperature dependence, which is presented in Figure 3. The single, time-averaged edt resonance observed at 65 °C broadens as the temperature is lowered and reemergences as two equally intense resonances below the coalescence temperature of 32 °C ($T_c(1)$). These become increasingly sharp until −21 °C, where the two singlets at 16.3 and 36.4 ppm have a line width of $\nu_{1/2}$ = 36.8 Hz. Below this temperature, these resonances begin to broaden. The upfield peak collapses at −51 °C ($T_c(2)$) and is followed by the downfield peak at −63 °C ($T_c(3)$). Each reappears as two lines of equal intensity. Thus, the single edt resonance at 65 °C results in splitting into two, three, and finally four peaks upon lowering the temperature. In the limiting spectrum at −70 °C, the four singlets come at 12.2 ($\nu_{1/2}$ = 76.7), 29.4 (76.7), 44.1 (79.6), and 47.0 ppm (90.9 Hz) with the intensity ratio of 1:1:1:1. All spectral changes are reversed upon raising the temperature and are independent of concentration.

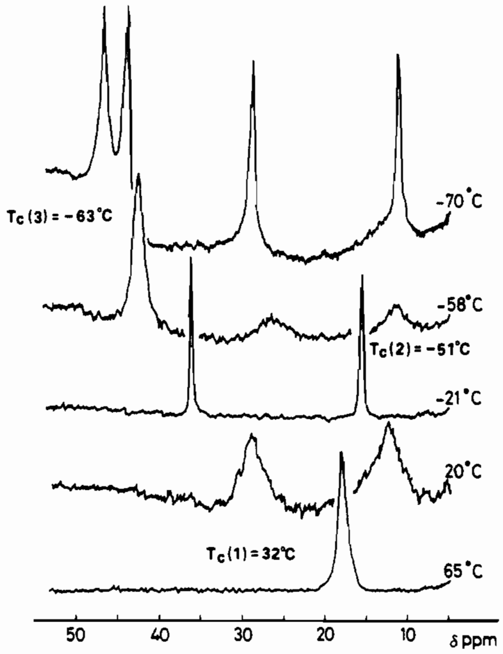


Figure 3. Variable-temperature ^{1}H NMR spectra (90 MHz, in THF-d_8) of **1** in the edt proton region. Experimentally determined coalescence temperatures are also given.

The large chemical shifts observed for the edt resonances are due to the paramagnetism of uranium(IV) to which the edt ligands are bound. The effects of the paramagnetism upon the ^{1}H NMR spectra will be discussed shortly, but first we examine the solution structure and the possible dynamical processes.

The appearance of four well-separated singlets in the −70 °C spectrum, presumably at a near slow-exchange limit, is most simply interpreted in terms of the presence of a single DD stereoisomer, *mmmm*-D_{2d}, in which all four protons within each edt ligand are nonequivalent. The four proton environments arise from nonequivalence of two sulfur coordination sites and from adoption of an envelope $\overline{\text{USCCS}}$ ring conformation. Thus, the solid-state DD structure of **1** is thought to be retained in solution.

Of the other five possible DD stereoisomers, two (*mmgg*-C_2 and *abmg*-C_1) may be ruled out on the basis of the number of the observed resonance lines. Also ruled out are two out of three stereoisomers of the square-antiprismatic (SAP) polyhedron (*llll*-D_4 and *llss*-C_2). For edt chelates, *llll*-D_4 should have only two nonequivalent protons, while for *mmgg*-C_2, *abmg*-C_1, and *llss*-C_2 more than four different types of protons should exist. From the number of peaks alone none of the remaining three DD structures (*gggg*-D_2, *gggg*-S_4, and *aabb*-D_2) or SAP *ssss*-D_2 can be excluded, but we prefer the *mmmm*-D_{2d} geometry to the above stereoisomers due to the size of the paramagnetic shifts as will be described later (see ref 18 for the designation of edges and vertices).

We see, in Figure 3, coalescence occurring at three different temperatures between −70 and 65 °C. Using the experimentally determined T_c values together with the chemical shift difference between the two sites at T_c in the absence of exchange, $\Delta\nu$, which was estimated according to the method described in the footnote,[40]

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(37) (a) Bonds, W. D., Jr.; Archer, R. D.; Hamilton, W. C. *Inorg. Chem.* **1971**, *10*, 1764–1773. (b) Archer, R. D.; Donahue, C. J. *J. Am. Chem. Soc.* **1977**, *99*, 269–271.

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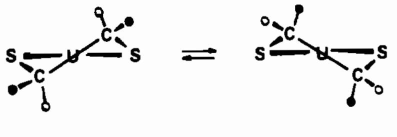
(39) (a) Titze, H. *Acta Chem. Scand.* **1970**, *24*, 405–414. (b) Steffen, W. L.; Fay, R. C. *Inorg. Chem.* **1978**, *17*, 779–782.

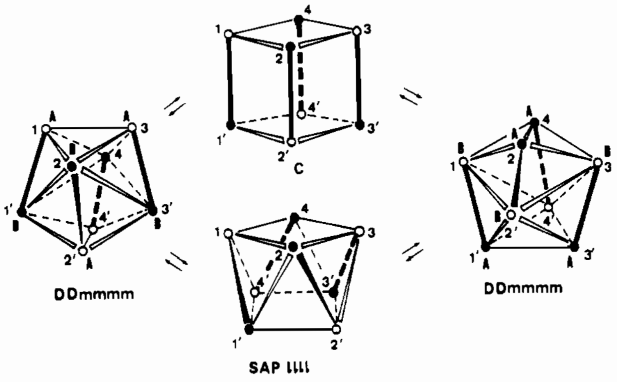
we obtained free energies of activation ΔG^* to be 12.9 kcal/mol ($T_c(1)$), 9.3 kcal/mol ($T_c(2)$), and 9.6 kcal/mol, ($T_c(3)$). The last two parameters may represent two independent observations of a single kinetic process, and therefore, we are seeing only two types of environmental averaging processes over the accessible temperature range.

Reasonable candidates for these are (1) conformational flexing of the USCCS chelate rings, illustrated in M, which equilibrate



M

the H_{ax} and H_{eq} geminal protons, and (2) exchange of sulfurs between the A and B sites, which serves to interchange the CH_2 groups within the edt ligand. The second dynamic process is illustrated in N, emphasizing two limiting pathways, one with a cubic transition state and the other with an SAP *llll* transition state. A simultaneous wagging motion of the four edt ligands generates a cubic transition state from DD and vice versa. The route via an SAP *llll* involves a further pinwheel distortion compared with the simpler cubic pathway. The sophisticated Hoard–Silverton mechanism is closely related to this SAP route, where the site-exchange path for DD *mmmm* traverse the SAP *ssss*, DD *gggg*, and SAP *llll* way points.[18,36b] Of the two routes in N, the SAP transition state is favored sterically.



N

From the ^{1}H NMR spectra alone, it is not possible to clearly decide which of the two fluxional mechanisms, M or N, corresponds to the high-temperature (or to the low-temperature) process. However, there are some clues in the energy barriers that have been measured for sulfur inversions, for conformational changes of MSCCS rings, and for polytopal rearrangement of tris- and tetrakis chelates. Some of these data are listed in Table VII.

Barriers to pyramidal inversion at the coordinated sulfur atoms in 1,2-bis(alkylthio)ethane complexes range ΔG^* = 10.7 kcal/mol for $Mo(CO)_4(PhCH_2SCH_2CH_2SCH_2Ph)$ to 19.5 kcal/mol for *cis*-$PtCl_2(MeSCH_2CH_2SMe)$.[41] In contrast, ring conformational changes like the one shown in M have extremely low barriers and are rarely observed. For instance, the elegant ^{1}H NMR study on ethane-1,2-dithiolate and propane-1,2-dithiolate complexes of Sn(IV) gave low ΔG^* values of 7.2–7.6 kcal/mol for such a ring inversion.[42] For $PtI_2[MeSCH(CF_3)CH(CF_3)SMe]$, a conformational change of the PtSCCS ring was postulated to be much faster than sulfur inversion.[43] We have also found in the NMR study of $[M(ndt)_3]^-$ (ndt = norbornane-*exo*-2,3-dithiolate; M = Nb, Ta) that the MSCCS ring reversal must occur with energies appreciably lower than that of the polytopal rearrangement between the synclastic and anticlastic geometrical isomers (ΔG^* = 12.6–13.7 kcal/mol).[7f,g] In the case of $[Nb(SCH_2CH_2S)_3]^-$, only one of the two possible fluxional processes, conformational change of the five-membered ring or racemization of the NbS_6 frame, was found to freeze out at low temperatures (ΔG^* = 9.2 kcal/mol).[44] On the other hand, the activation free energies ΔG^* (T_c) for A- and B-site exchange processes of $[Nb(S_2CNMe_2)_4]Cl$, $[Ta(S_2CNR_2)_4][TaCl_6]$, $[M(OSCNMe_2)_4][MCl_6]$ (M = Nb, Ta), and $M(OSCNMe_2)_4$ (M = Ti, Zr) are 10.16, 11.05–11.50, 14.10–14.70, and 9.88–11.25 kcal/mol, respectively.[36]

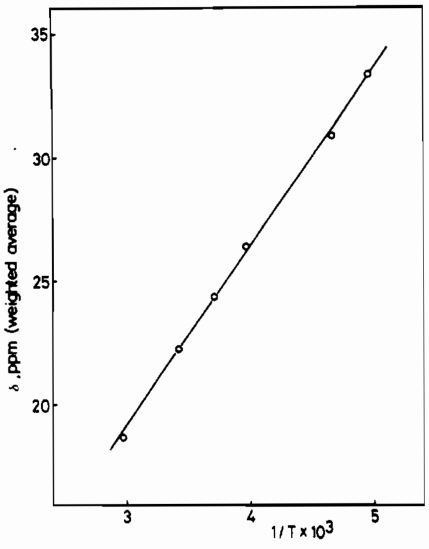


Figure 4. Weighted averages of edt proton chemical shifts plotted as a function of 1/*T*.

Considering these energy data, it is very likely that the metal-centered rearrangement of the DD structure is a higher energy motion than the conformational change of the five-membered MSCCS rings. Thus, we may reasonably assume that the high-temperature process observed for **1** corresponds to the exchange between A and B sites and that the low-temperature process is in turn the ring reversal. The estimated barrier (ΔG^* = 9.3–9.6 kcal/mol) to the latter appears to be at the upper limit of such conformational changes. The occurrence of Li bridges between S atoms would raise the barrier to ring flipping motion, and perhaps it may also affect the site exchange process. Note that the polytopal rearrangements within the SAP and BTP structures

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(40) The separation of the nonexchanging proton peaks, $\Delta\nu$, is temperature dependent due to the paramagnetism of **1**. It was suggested that $\Delta\nu$ at the coalescence temperature could be obtained by extrapolation of proton chemical shifts to T_c. We have estimated the $\Delta\nu$ values at $T_c(1)$ and $T_c(2)$, according to this method, from the linear plots of the corresponding proton peaks vs 1/*T* in the temperature ranges −70 °C ~ 0 °C and −70 °C ~ −60 °C, respectively. This method could not be applied for $\Delta\nu$ at $T_c(3)$, because low-temperature spectra below −70 °C are lacking, and thus we employed the $\Delta\nu$ value at −70 °C. Although this method produces a rather large error in $\Delta\nu$, it affects the resulting ΔG^* values only slightly. We estimate the probable error in ΔG^* to be less than ±0.2 kcal/mol: (a) Ho, F. F.-L.; Reilley, C. N. *Anal. Chem.* **1970**, *42*, 600–605. (b) Cramer, R. E.; DeRyke, R. *Can. J. Chem.* **1973**, *51*, 892–896.

(41) (a) Abel, E. W.; Bhargava, S. K.; Orrell, K. G. *Prog. Inorg. Chem.* **1984**, *32*, 1–118. (b) Cross, R. J.; Hunter, G.; Massey, R. C. *J. Chem. Soc., Dalton Trans.* **1976**, 2015–2017. (c) Abel, E. W.; Khan, A. R.; Kite, K.; Orrell, K. G.; Šik, V. *J. Chem. Soc., Dalton Trans.* **1980**, 1175–1181. (d) Abel, E. W.; Bhargava, S. K.; Bhatti, M. M.; Kite, K.; Mazid, M. A.; Orrell, K. G.; Šik, V.; Williams, B. L.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 2065–2072. (e) Abel, E. W.; Bhargava, S. K.; Kite, K.; Orrell, K. G.; Sik, V.; Williams, B. L. *Polyhedron* **1982**, *1*, 289–298.

(42) Abel, E. W.; Bhargava, S. K.; Orrell, K. G.; Šik, V. *J. Chem. Soc., Dalton Trans.* **1982**, 2073–2078.

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(44) Martin, J. L.; Takats, J. Submitted for publication. We thank Joe Takats for providing us his variable-temperature ^{1}H NMR results before publication.

Table VII. Energy Barriers to Internal Molecular Motions for S–S Chelated Metal Complexes

complex	dynamical process	$\Delta G^{\ddagger}$, kcal/mol	ref
$Mo(CO)_4(PhCH_2SCH_2CH_2SCH_2Ph)$	sulfur inversion	11.7 (300 K)	41b
$ReCl(CO)_3(MeSCH_2CH_2SMe)$	sulfur inversion	15.6 (298 K)	41d
$PtCl_2(MeSCH_2CH_2SMe)$	sulfur inversion	19.5 (298 K)	41e
$PtClMe_3(MeSCH_2CH_2SMe)$	sulfur inversion	15.1 (298 K)	41c
$SnMe_2(SCH_2CH_2S)$	ring conformational change[a]	7.6 (298 K)	42
$SnMePh(SCH_2CH_2S)$	ring conformational change	7.6 (298 K)	42
$SnMe_2[SCH(Me)CH_2S]$	ring conformational change	7.2 (298 K)	42
$[Et_4N][Nb(ndt)_3]$[b]	isomerization[c]	12.6 (303 K)	
	ring conformational change	≪12.6	7f
$[Ph_4P][Ta(ndt)_3]$	isomerization	13.7 (303 K)	
	ring conformational change	≪13.7	7f
$[Ph_4As][Nb(SCH_2CH_2S)_3]$	trigonal twist of NbS_6 or ring conformational change	9.2 (195 K)	44
$[Nb(S_2CNMe_2)_4]Cl$ (DD)[d]	A- and B-site exchange	10.2 (197 K)	36c
$[Ta(S_2CNMe_2)_4][TaCl_6]$ (DD)	A- and B-site exchange	11.1 (211 K)	36a
$[Nb(OSCNMe_2)_4][NbCl_6]$ (DD)	A- and B-site exchange	14.7 (258 K)	36c
$Zr(OSCNMe_2)_4$ (DD)	A- and B-site exchange	11.3 (220 K)	36b
$U(acac)_4$ (BTP)[e]	polytopal rearrangement	5.4 (163 K)	38
$Zr(acac)_4$ (SAP)	polytopal rearrangement	7.2 (163 K)	38
$[Li(dme)]_4[U(SCH_2CH_2S)_4]$ (DD)	A- and B-site exchange	12.9 (305 K)	this work
	ring conformational change	9.3 (222 K)	this work

[a] Conformational change within $\overline{\text{MSCCS}}$ chelate rings. [b] Ndt = norbornane-*exo*-2,3-dithiolate. [c] Isomerization between synclastic and anticlastic geometries associated with the unsymmetric nature of the ndt ligand in the direction perpendicular to the MS_2 plane. [d] DD = dodecahedron. [e] BTP = bicapped trigonal prism with the $h_1h_1p_2p_2$-C_2 chelate-ligand wrapping pattern. The polytopal rearrangement is thought to proceed in terms of interconversion between the square and diamond faces of the BTP.

of $Zr(acac)_4$ and $U(acac)_4$ are notably faster than site exchange within the DD structures.[38]

Early in this section, we have already mentioned the large paramagnetic shifts of the edt resonances. It has been noticed that ligand proton chemical shifts of U(IV) complexes often exhibit approximate Curie behavior.[45] For complex **1** such was the case, and the weighted average of the edt proton chemical shifts at each temperature correlates linearly with $1/T$ (K), as shown in Figure 4. Furthermore, the intercept at $1/T = 0$ is −6 ppm, which is close to the expected value. These facts support our assignment of the NMR signals. To take a closer look at the size of paramagnetic shifts, we have calculated the isotropic shifts, using the edt proton resonance (δ = 3.7 ppm, in DMSO-d_6) of $[A][Nb(edt)_3]$ (A = Li, Et_4N, Ph_4P)[7c,d] as a diamagnetic standard. Thus, the four singlets in the −70 °C spectrum have downfield isotropic shifts Δ^{iso} of −8.5, −25.7, −40.4, and −43.3 ppm.[46]

Rigorous evaluation of the contribution of the contact (hyperfine) and pseudocontact (dipolar) terms to the isotropic shifts is not an easy task in the present case. However, in view of the large difference in isotropic shifts among the four edt protons, it seems likely that the latter effect dominates over the former. In its general form, the dipolar shift can be expressed by $\Delta^{dip} = (3N)^{-1}[\chi_{\parallel} - \chi_{\perp}]G(\theta,r)$ in terms of susceptibility (χ) anisotropy,[47] if a molecule possesses a ligand field of axial symmetry, which is not a bad assumption at all for **1**. Here, $G(\theta,r)$ is the geometrical factor defined as $(3\cos^2\theta - 1)/r^3$, and the other terms may be regarded as a constant for a given temperature.

We have estimated the geometrical factor for the edt protons on the basis of a DD *mmmm* geometry with twisted edt ligands similar to the one used for the MO calculations earlier in this paper. In order to better mimic the X-ray-derived structure, the geometry is slightly modified such that the U–S(A) (2.885 Å) and U–S(B) (2.815 Å) distances are differentiated and the slight displacement of the S atoms from the trapezoidal planes is also duplicated. That gave $G(\theta,r)$ values of 0.0014 and −0.0045 Å^{-3} for the A-site protons and −0.0086 and −0.010 Å^{-3} for the B-site protons. The correlation with the observed isotropic shifts is acceptable considering the approximate nature of our analysis, but still bothersome is the fact that the sign of one isotropic shift is reversed. This discrepancy can be resolved by expanding the two S(A)–U–S(A) angles by around 7° from the observed 63°. Then the $G(\theta,r)$ values become −0.0017 (H(A)), −0.0077 (H(A)), −0.0091 (H(B)), and −0.012 Å^{-3} (H(B)), which can be converted to Δ^{iso} = −6.6 (H(A)), −30 (H(A)), −36 (H(B)), and −46 (H(B)), respectively, by using a common constant of $(3N)^{-1}[\chi_{\parallel} - \chi_{\perp}] = 3920$.[48] The agreement with the observed isotropic shifts is now satisfactory. It is noteworthy that according to our calculations of dipolar shifts the two upfield resonances arise from the A-site protons and the two downfield resonances from the B-site protons. This result is fully consistent with our interpretation of the variable-temperature ^{1}H NMR spectra in that the low-temperature process, which equilibrates these pairs of resonances, is attributable to the ring conformational change as depicted in M.

There is no direct proof that this kind of slight geometrical change from the crystal structure actually occurs in solution. Nonetheless, we feel comfortable in suggesting this possibility, because our overlap population analysis on G–I indicates rather large repulsive nonbonding interactions between the neighboring S(A) atoms (see Table VI) that could be eased by opening up of the S(A)–U–S(A) angles. The good agreement between observed and calculated paramagnetic shifts as well as consistency between the peak assignment and the interpretation of dynamical processes also supports this hypothesis.

Reaction with CS_2. Insertion of carbon disulfide into f-element amide bonds has been shown to yield the ubiquitous dithiocarbamates.[49] Although such an insertion into actinide-to-sulfur bonds has not been reported, reaction of CS_2 with the MoS_4 moiety in $[(S_4)_2MoS]^{2-}$ and $[(S_4)_2Mo_2(S)_2(\mu\text{-}S)_2]^{2-}$ and with the analogous NiS_4 moiety in $[Ni(S_4)_2]^{2-}$ resulted in formation of the

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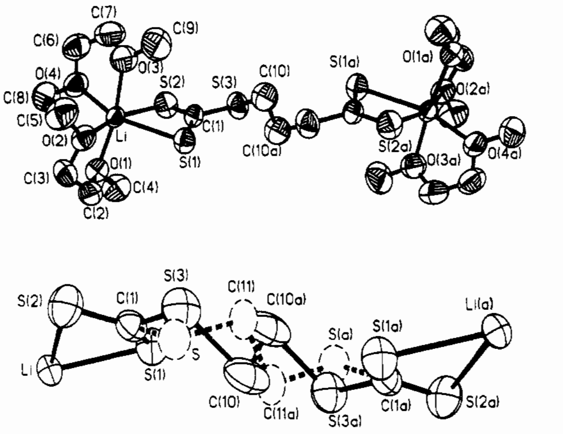


Figure 5. Perspective drawing of $[Li(dme)_2][S_2CSCH_2CH_2SCS_2]$ (**2**), drawn at the 50% probability level, with the atom-labeling scheme: (top) entire molecule where only one of the two sets of disordered atoms, i.e., S(3) and C(10) (66% occupancy), is included; (bottom) ethane-1,2-diyl bis(trithiocarbonate) portion including all disordered atoms, where S and C(11) are complements of S(3) and C(10), respectively.

intriguing $\overline{\mathrm{MSSC(S)S}}$ ring.[50] It was of interest to examine a reaction of the uranium edt complex $[Li(dme)]_4[U(SCH_2CH_2S)_4]$ (**1**) with CS_2.

Thus, **1** was allowed to react with excess CS_2 in DME. Immediate precipitation of a yellow-brown solid occurred, while the color of the solution turned from pale green to yellow. From the resulting DME solution we were able to isolate a lithium salt of ethane-1,2-diyl bis(trithiocarbonate), $[Li(dme)_2]_2(S_2CSCH_2CH_2SCS_2)$ (**2**) as yellow needles in 33% yield based on Li. Characterization of **2** was done straightforwardly by UV-visible, ^{1}H NMR, and IR spectra,[51,52] and its structure determination by X-ray crystallography proved the formulation of **2** to be correct. **2** was the single product isolated from the DME solution, and no uranium complex was detected in that phase.

$$\underset{\mathbf{1}}{[Li(dme)]_4[U(SCH_2CH_2S)_4]} \xrightarrow[\text{in DME}]{CS_2\ \text{(excess)}}$$

$$\underset{\mathbf{2}}{[Li(dme)_2][S_2CSCH_2CH_2SCS_2]} + \text{yellow-brown solid}$$

yellow orange crystals
yield 33%

The yellow-brown solid is air- and/or moisture-sensitive, and apparently it contains both uranium and lithium. The uranium-containing products or product is practically insoluble in organic and O-donor solvents. We presume it has a polymeric structure having ethene-1,2-diyl bis(trithiocarbonate) as an anchor ligand, which may be tentatively formulated as $Li_{2x-4}U(S_2CSCH_2CH_2CS_2)_x$ ($2 < x \lesssim 4$). However, whether the edt ligands are completely converted into bis(trithiocarbonate) ligands remains to be determined. Recently, M_2(edt) compounds (M = Li, Na, K, etc.) were reported to take up CS_2 to give the corresponding ethane-1,2-diyl bis(trithiocarbonates).[51] Thus, CS_2 is capable of being inserted into Li–S bonds. As for the reaction of **1**, an interesting question arises as to whether the initial CS_2 insertion step occurs at Li–S bonds or at U–S bonds or both. It is interesting that the Nb analogue of **1**, $[Li(thf)_4][Nb(edt)_3]$, does not react with CS_2.

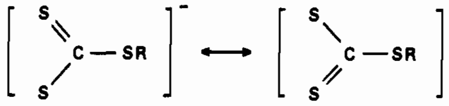
Two perspective drawings of the structure of **2** are presented in Figure 5, which illustrate the numbering scheme as well. Selected bond distances and angles are given in Table VIII.

Table VIII. Selected Bond Distances (Å) and Bond Angles (deg) for $[Li(dme)_2]_2[S_2CSCH_2CH_2SCS_2]$ (**2**) with Esd's in Parentheses

Li–S(1)	2.699 (6)	Li–S(2)	2.794 (6)
Li–O(1)	2.184 (7)	Li–O(2)	2.133 (6)
Li–O(3)	2.234 (7)	Li–O(4)	2.063 (6)
S(1)–C(1)	1.671 (4)	S(2)–C(1)	1.672 (4)
S(3)–C(1)	1.77 (1)	S–C(1)	1.82 (1)
S(3)–C(10)	2.26 (3)	S–C(10)	2.04 (3)
S(3)–C(11)	1.65 (3)	S–C(11)	1.92 (3)
C(10)–C(10a)	1.34 (4)	C(11)–C(11a)	1.71 (5)
S(1)–Li–S(2)	65.8 (1)	S(1)–Li–O(1)	94.3 (2)
S(1)–Li–O(2)	99.4 (2)	S(1)–Li–O(3)	93.6 (2)
S(1)–Li–O(4)	158.2 (3)	S(2)–Li–O(1)	99.0 (2)
S(2)–Li–O(2)	164.6 (3)	S(2)–Li–O(3)	92.1 (2)
S(2)–Li–O(4)	95.1 (2)	O(1)–Li–O(2)	76.9 (2)
O(1)–Li–O(3)	168.3 (3)	O(1)–Li–O(4)	99.4 (3)
O(2)–Li–O(3)	93.2 (2)	O(2)–Li–O(4)	100.2 (3)
O(3)–Li–O(4)	75.8 (2)		
S(1)–C(1)–S(2)	126.6 (3)	S(1)–C(1)–S(3)	121.6 (3)
S(2)–C(1)–S(3)	111.2 (3)	S–C(1)–S(1)	121.4 (4)
S–C(1)–S(2)	109.9 (4)		

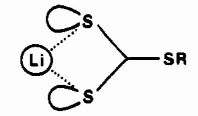
The structure analysis shows that crystals of **2** are composed of discrete, monomeric $[Li(dme)_2]_2(S_2CSCH_2CH_2SCS_2)$ molecules. A crystallographically imposed inversion center resides in the middle of the zigzag bis(trithiocarbonate) skeleton and each trithiocarbonate coordinates to lithium in an η^2 manner. The methylene carbon C(10) and the sulfur S(3) to which C(10) is bonded are disordered with an occupancy factor of 0.66 (3), and their complements are labeled as S and C(11), respectively. Thus, a trithiocarbonate consists of either C(1), S(1), S(2), and S(3) or C(1), S(1), S(2), and S; both of these four atom groups are individually coplanar to within 0.06 Å (and 0.11 Å). The lithium sits 0.79 Å (and 1.45 Å) above their mean planes. Alternatively, the out-of-plane displacement of Li can be incarnated in the dihedral angles between these trithiocarbonate planes and the LiS(1)S(2) coordination plane, which are 159.4 and 142.3°. The observation of disorder indicates that the particular orientation of Li with respect to the trithiocarbonate plane has only minor energetic consequences.

Despite the limitations in accuracy of the metric parameters imposed by the disorder for the trithiocarbonate moiety, there is a meaningful difference in the C–S bond distances. The "outer" C–S(1,2) bonds are shorter by ca. 0.1 Å than the "inner" C–S(3) and C–S bonds, which is in agreement with the resonance forms shown in O.



O

The Li ion adopts a distorted octahedral configuration surrounded by two sulfur atoms of a thiocarbonate and four oxygen atoms of dme molecules, which contrasts to the tetrahedral LiS_2O_2 array in complex **1**. The Li–S distances (average 2.747 Å) are evidently longer than those of **1** (average 2.42 Å). The weak Li–S interactions in **2** can be explained partly by the orientation of a lone pair on each sulfur atom of the S_2CS- chelating ligand, particularly those in the a_1 type molecular orbital, P, arising from



P

in-phase combination of such lone pairs. In the a_1 orbital, the orbital lobes deform outward from the lines drawn between Li and the sulfur atoms. Thus, the sulfur lone pairs are unable to assume the best orientation toward a Li atom, which leads to poorer Li–S orbital overlap. The theoretical analysis on the effects

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similar to the above has been given for the very long U-C bond lengths in the phosphoylide complex $(C_5H_5)U[(CH_2)(CH_2)PPh_2]$.[53]

Alternatively, the Li-S bond elongation may be interpreted by the larger coordination number of **2**. Thus, also longer are the Li-O distances of 2.154 Å (average) relative to 2.06 Å (average) for **1**, albeit the difference is less significant in this case. Within the LiS_2O_4 coordination sphere of **2**, the Li-O(2,4) bond lengths trans to sulfur atoms are shorter by 0.11 Å (average) than the Li-O(1,3) distances as a consequence of the weak Li-S coordination.

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Supplementary Material Available: For **1** and **2**, tables of crystal data (Table S1), complete anisotropic and isotropic temperature factors of non-hydrogen atoms (Tables S2 and S5), and hydrogen atom parameters (Tables S3 and S6) (5 pages); listings of observed and calculated structure factors (Tables S4 and S6) (22 pages). Ordering information is given on any current masthead page.

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Experimental Evidence for Comparable Strength of P-S and P-N pπ-Bonding within the Heteronaphthalenic Framework: Spectroscopic and Structural Studies of the 1,3,2-Benzazathiaphospholium System as a Cation and as Neutral Halides

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The new heteronaphthalenic framework 1,3,2-benzazathiaphospholium has been prepared as a free cation **1**[NSP] and as the neutral chloride **2**[NSPCl] and bromide **2**[NSPBr] derivatives. The spectroscopic and structural (crystal data for $C_6H_5AlCl_4NPS$: monoclinic, $P2_1/c$, a = 6.4773 (6) Å, b = 23.5434 (21) Å, c = 8.5101 (6) Å, β = 98.048 (7)°, Z = 4) features of the cation are consistent with a hybrid of the corresponding dithia **1**[S_2P] and diamino **1**[N_2P] derivatives. In particular, the P-N and P-S bond lengths are very similar to those of the parent cations and represent experimental evidence for P-N and P-S pπ-bonding of comparable strength, in agreement with the theoretical π-bond energies. The neutral halides, 2-chloro-1,3,2-benzazathiaphosphole (crystal data for C_6H_5ClNPS: monoclinic, $P2_1/c$, a = 8.5607 (10) Å, b = 10.6948 (10) Å, c = 8.5994 (13) Å, β = 95.516 (11)°, Z = 4) and 2-bromo-1,3,2-benzazathiaphosphole (crystal data for C_6H_5BrNPS: monoclinic, $P2_1/c$, a = 8.5345 (12) Å, b = 10.6990 (14) Å, c = 8.8213 (7) Å, β = 94.705 (8)°, Z = 4) are isostructural and adopt dimeric structures, with long P-Z bonds. Moreover, the heterocyclic units are close to planar demonstrating an inherent thermodynamic stability for the heteronaphthalenic framework. Consequently the covalent halides **2** can be considered partially ionic, intermediate between that of the ionic salts and a purely covalent system, or a weak Lewis adduct of the cation **1** and a halide.

Introduction

The second-row non-metal elements (B, C, N, O, F) are unique in their ability to form strong pπ-bonds with many elements. Sulfur is often included in this category and theoretical pπ bond strengths for atoms bound to sulfur are comparable with those of the same elements bound to nitrogen (e.g. P=N 44, P=S 40 kcal mol^{-1}).[2] In this context, we have recently reported the preparation and characterization of a number of components that contain the first examples of stable pπ-bonding between sulfur and the heavier elements of group 15.[3-7] The new systems (**1**[S_2P], **1**[S_2As], **1**[S_2Sb], and **1**[NSAs]) are derivatives of the cationic heteronaphthalenic framework **1**, and demonstrate the ability of sulfur to achieve effective pπ-overlap. The stability of such systems is reliant upon a Huckel number of π-electrons, and effective pπ-delocalization of molecular charge is illustrated by dramatic deshielding of the ^1H and ^{13}C NMR signals for the aromatic ring. This is consistent with the parent carbon derivatives (e.g. 1,3-benzodithiolium (**1**[S_2C])[8] and 1,3-benzothiazolium (**1**[NSC])[9] cations) and the nitrogen derivative (1,3,2-benzodithiazolium cation (**1**[S_2N]).[10,11] Furthermore, molecular planarity is observed in structural studies of **1**[S_2N],[10b,11] **1**[S_2P],[3,4] **1**[NSAs][7] and the diamino- derivative **1**[N_2P],[12] confirming the incorporation of the heteroatomic centers into the pπ-structure. Consequently, **1** represents a servicable synthetic template for the potential general development of pπ-bonding arrangements for the heavier non-metals. We now emphasize the versatility of this template, with the preparation and characterization of 1,3,2-benzazathiaphospholium (**1**[NSP]) tetrachloroaluminate. The new cation **1**[NSP] is a hybrid of the benzodithiaphospholium **1**[S_2P][3-6] and benzodiazaphospholium **1**[N_2P][12] systems and allows for a direct experimental comparison between P-S and P-N pπ-bonding. In addition, we compare the spectroscopic and structural features of the neutral covalent chloride **2**[NSPCl] (2-chloro-1,3,2-benzazathiaphosphole) and bromide **2**[NSPBr] (2-bromo-1,3,2-benzazathiaphosphole) systems. The heterocyclic units in these halides are structurally similar to that of the free

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