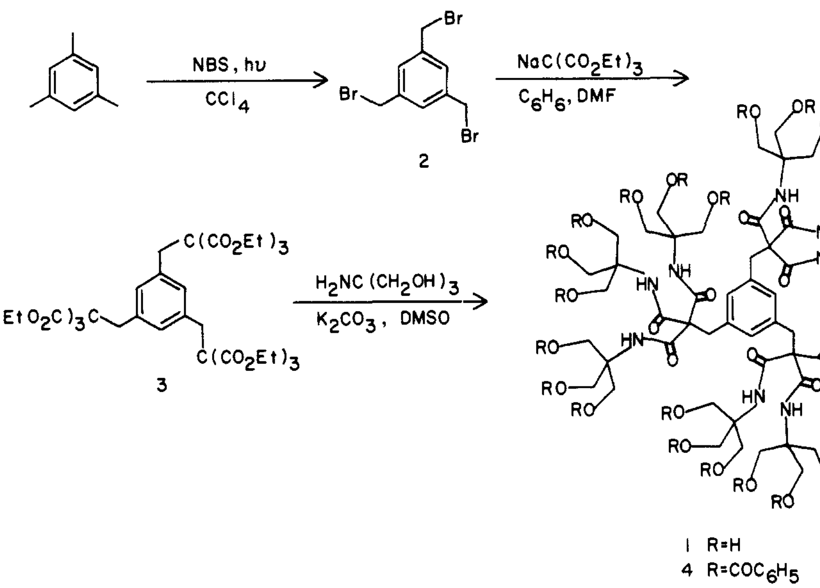
Scheme I



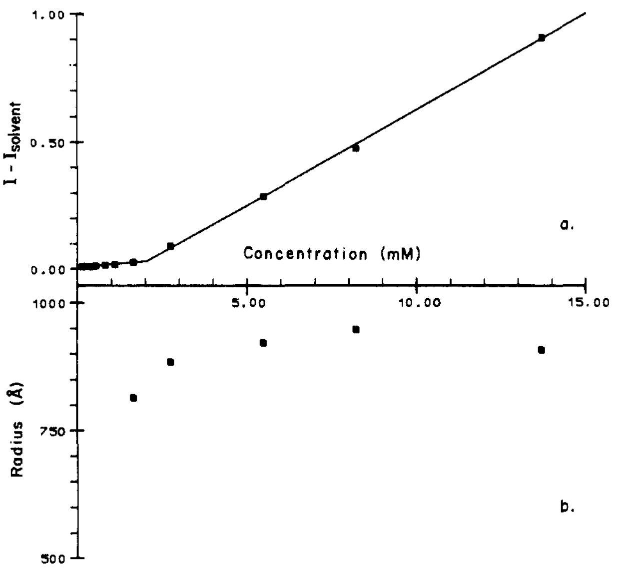


Figure 4. (a) Concentration dependence of the intensity of scattered light (scattering angle $\theta = 90°$). The lines shown use the result of a least-squares fit with $m = 6175$, $b = 8478$, and $r^2 = 0.967$ and $m = 40656$, $b = -61017$, and $r^2 = 0.999$ for the data from 0.137 to 1.64 mM and from 2.74 to 13.7 mM, respectively (cmc = 2.02 mM). (b) Concentration dependence of the calculated Stokes radius. Values below 1.0mM showed signs of an insufficient number of particles in the sample volume and have been omitted.

of **1** appear as light areas (~200-Å diameter) against a darker background. Close examination of Figure 2 reveals the triangular arrangement of cascade spheres visible on the surface of the aggregate. Calculations using dimensions determined from molecular models indicate ca. 40 molecules of arborol **1** per aggregate (Figure 2, e.g., aggregate A). Figure 3 shows a TEM of a higher concentration region where microcrystals of arborol **1** have formed.

The micellar character of aggregates of **1** was also evaluated by light scattering experiments. The intensity of scattered light ($\theta = 90°$), as a function of concentration, is shown in Figure 4a. The change in scattered intensity at a concentration of 2.02 mM is indicative of the critical micelle concentration (cmc). Dynamic light scattering gives a Stokes radius for the aggregate of ca. 950 Å (Figure 4b) and shows only minor dependence on concentration above CMC.

Development and exploitation of these new polymeric cascades are in progress.

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Supplementary Material Available: Experimental, electron microscopy, and light-scattering details (3 pages). Ordering information is given on a current masthead page.

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(10) The initial concentration of **1** was below the cmc; however, aggregation occurred upon concentration during drying.

Preparation of a Novel Sulfur-Nitrogen Cage Compound by the Transamination of Bis(dimethylamino) Sulfide with a Macrocyclic Tetrakis(secondary amine)

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Transamination of tris(dimethylamino)phosphine with the macrocyclic tetrakis(secondary amine) 1,4,7,10-tetraazacyclododecane ("cyclen") results in oxidative addition of one of the N-H bonds to the trivalent phosphorus atom to give the pentavalent phosphorus-hydrogen compound $C_8H_{16}N_4PH$[1,2] which is an important synthetic entry to other phosphorus(V) derivatives exhibiting novel structural features.[3,4] This paper reports the transamination of bis(dimethylamino) sulfide with the same macrocyclic tetrakis(secondary amine). This reaction not only proceeds totally differently from the corresponding reaction of tris(dimethylamino)phosphine but gives an unexpected and unprecedented type of sulfur-nitrogen cage compound.

In a typical experiment 5.0 g (29 mmol) of 1,4,7,10-tetraazacyclododecane[5] is boiled under reflux in 35 mL of bis(di-

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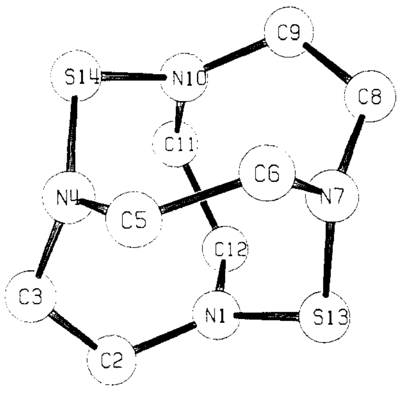

Figure 1. Structure of $C_8H_{16}N_4S_2$. Hydrogen atoms of the methylene groups are omitted for clarity.

methylamino) sulfide[6] for about 1 h until the color of the solution turns from yellow to red. Cooling the concentration in vacuum gives a total of 4.0–5.5 g (60–80% yield) of colorless crystalline air-stable $C_8H_{16}N_4S_2$. The analytical sample, mp 170 °C,[7] can be purified by vacuum sublimation at 110–120 °C (0.5 mm) or by recrystallization from methanol or chloroform. Similar reactions of 1,4,8,11-tetraazacyclotetradecane ("cyclam") and *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane[8] with bis(dimethylamino) sulfide give white $C_{10}H_{20}N_4S_2$, mp 175 °C, and white $Me_6C_{10}H_{14}N_4S_2$, mp, 195 °C, respectively.[7]

The compound $C_8H_{16}N_4S_2$ forms orthorhombic crystals by sublimation: space group *Pbcn*; $a = 11.367$ (2) Å, $b = 8.278$ (3) Å, $c = 11.266$ (2) Å; $Z = 4$; $d_{\text{calcd}} = 1.45$ g/cm³. The structure was solved by direct methods.[7] Least-squares refinement[7] using the 861 observed ($I > 3\sigma_I$) reflections after application of Lorentz–polarization corrections revealed the structure depicted in Figure 1 ($R = 0.080$ and $R_w = 0.085$).

The structure of $C_8H_{16}N_4S_2$ (Figure 1) exhibits a number of interesting features. Its topology is that of a tetrahedron in which the four vertices are occupied by nitrogen atoms, four of the six edges by $-CH_2CH_2-$ bridges, and the remaining two edges by sulfur atoms. This pattern of substitution reduces the symmetry of the tetrahedron from T_d to C_2 with the C_2 axis bisecting the C_5–C_6 and C_{11}–C_{12} bonds; this C_2 axis is also the C_2 axis of the space group *Pbcn*. The coordination at each nitrogen atom is nearly planar with the sums of the three bond angles at the nonequivalent nitrogen atoms N_1 and N_7 being 358.3° and 357.4°, respectively. The N–S–N bond angles are 117.2° and the S–N bond distances fall in the range 1.655–1.657 Å. These parameters compare with the N–S–N bond angles of 114.5°, 113.2°, and 110.7° and S–N bond distances of 1.688, 1.678, and 1.657 Å found by electron diffraction on bis(dimethylamino) sulfide[9] and by X-ray diffraction on dimorpholino sulfide[10] and bis(dicyclohexylamino) sulfide,[11] respectively, indicating relatively little effect of the cage structure on these important structural parameters.

The size of the approximate tetrahedral cavity in $C_8H_{16}N_4S_2$ formed by the nitrogen atoms is indicated by the three unique N–N distances: N_1–N_7 2.74, N_1–N_4 2.94, and N_1–N_{10} 2.98 Å. Each of these distances corresponds to two of the six edges of the distorted N_4 tetrahedron in $C_8H_{16}N_4S_2$. Assuming an average tetrahedral edge length of 2.89 Å and a covalent radius of 0.75 Å for nitrogen,[12] the largest sphere that can be contained in the cavity has a radius of 1.0 Å. Thus a potassium ion with an ionic radius of 1.33 Å is too large to occupy the cavity but lithium and sodium ions with radii of 0.60 and 0.95 Å, respectively, are candidates for incorporation into the cavity.

The proton and carbon-13 NMR spectra of $C_8H_{16}N_4S_2$ in $CDCl_3$ at ambient temperatures each exhibit single resonances at δ 3.46 and 56.7, respectively, indicating equivalence of all eight carbons and all 16 hydrogens on the NMR time and resolution scales. The mass spectrum of $C_8H_{16}N_4S_2$ exhibits not only the expected molecular ion but also the fragment ions $C_8H_{16}N_4^+$, $C_4H_8N_2S_2^+$, $C_4H_7N_3S^+$, $C_4H_9N_2^+$, $C_4H_8N_2^+$, $C_4H_7N_2^+$, $C_2H_4N_2^+$, and $C_2H_4N^+$.

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Supplementary Material Available: Tables of positional parameters and their estimated standard deviations, β's, and bond distances and angles and a drawing of the unit cell (4 pages). Ordering information is given on any current masthead page.

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Structure and Magnetic Properties of an Unsymmetrical (μ-Oxo)diiron(III) Complex

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(μ-Oxo)diiron(III) complexes have long been of considerable interest for their distinctive magnetic and spectroscopic properties[3] and relevance to diiron nonheme proteins such as hemerythrin,[4] ribonucleotide reductase,[5] and several purple acid phosphatases.[6] In contrast to other bridging ligands, where only weak antiferromagnetic coupling is observed, μ-oxo diiron(III) complexes show substantial coupling for which, with few exceptions, the values of J ($H = -2JS_1S_2$) lie in the remarkably narrow range of −90 to −110 cm⁻¹ regardless of the geometry of the Fe–O–Fe moiety and of the number of ligands (4, 5, 6, or 7). With the exception of hemerythrin,[9] in all these complexes the stereochemistry about the two iron atoms is identical. See Table I.[4,7-17]

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