Table II. Positional Parameters

atom	x	y	z
As	0.27017 (6)	0.21813 (4)	−0.02812 (5)
Zn	0.0	0.0	0.0
S(1)	0.3214 (2)	0.30332 (9)	0.5834 (1)
S(2)	0.2933 (1)	0.66605 (9)	0.1104 (1)
S(3)	0.0693 (2)	0.97872 (9)	0.3093 (1)
S(4)ᵃ	0.4679 (5)	0.9892 (4)	0.7677 (4)
S(4')ᵃ	0.4278 (6)	0.9901 (4)	0.7004 (5)
F(1)	0.3102 (4)	0.5950 (2)	0.5221 (3)
F(2)	0.1500 (5)	0.8356 (3)	0.5335 (4)
O(1)	0.1576 (4)	0.8777 (2)	0.0127 (3)
O(2)	0.0626 (5)	0.0234 (3)	0.1859 (3)
O(3)	0.3086 (7)	0.9748 (4)	0.7585 (5)
N(1)	0.2462 (5)	0.7006 (3)	0.9642 (3)
N(2)	0.3584 (5)	0.5506 (3)	0.0868 (3)
O(4)ᵃ	0.515 (2)	1.024 (1)	0.660 (1)
O(4')ᵃ	0.563 (2)	1.044 (1)	0.723 (1)

ᵃ Population 0.5.

Table III. Bond Distances (Å) and Angles (deg)

Zn-O(1) (2×)	2.070 (2)	S(3)-O(2)	1.468 (2)
Zn-O(2) (2×)	2.030 (2)	As-F(1)	1.756 (2)
Zn-F(1) (2×)	2.082 (2)	As-F(2)	1.687 (2)
S(1)-O(1)	1.475 (2)	S(4)-O(3)	1.341 (6)
S(1)-N(1)	1.514 (3)	S(4)-O(4)	1.39 (1)
S(2)-N(1)	1.641 (3)	S(4')-O(3)	1.310 (7)
S(2)-N(2)	1.647 (3)	S(4')-O(4')	1.32 (1)
S(3)-N(2)	1.513 (3)		

O(1)-Zn-O(1)	180.0	Zn-O(1)-S(1)	129.1 (1)
O(1)-Zn-O(2) (2×)	90.8 (1)	Zn-O(2)-S(3)	145.6 (2)
O(1)-Zn-O(2) (2×)	89.2 (1)	O(1)-S(1)-N(1)	115.5 (1)
O(1)-Zn-F(1) (2×)	91.6 (1)	N(1)-S(2)-N(2)	97.0 (1)
O(1)-Zn-F(1) (2×)	88.4 (1)	N(2)-S(3)-O(2)	112.7 (2)
O(2)-Zn-O(2)	180.0	S(1)-N(1)-S(2)	125.9 (2)
O(2)-Zn-F(1) (2×)	91.4 (1)	S(2)-N(2)-S(3)	123.3 (2)
O(2)-Zn-F(1) (2×)	88.6 (1)	Zn-F(1)-As	150.0 (2)
F(1)-Zn-F(1)	180.0	F(1)-As-F(2)	179.2 (1)
O(3)-S(4)-O(4)	116 (1)	O(3)-S(4')-O(4')	135 (1)

final refinement, including isotropic extinction, resulted in $R(F)$ = 0.051 and $R_w(F)$ = 0.059. These values are larger than expected from the quality of the data, due to the difficulty in describing the disordered atoms. The final difference synthesis did not show peaks exceeding 0.7 e/Å³. The atomic parameters are given in Table II.

Results and Discussion

The reaction of $[Zn(SO_2)_2](AsF_6)_2$ and $S(NSO)_2$ in a molar ratio of 1:2 in liquid SO_2 results in the formation of a complex with the composition $\{Zn[S(NSO)_2]_2\}(AsF_6)_2 \cdot 2SO_2$ (**1**). S-$(NSO)_2$ was prepared from $(CH_3)_3SiNSO$ and sulfur di-chloride.[4] **1** forms bright yellow crystals, which are stable under an SO_2 atmosphere but decompose in moist air. **1** starts to lose SO_2 at room temperature, which results in the decomposition of the surface and formation of $\{Zn[S(NS-O)_2]_2\}(AsF_6)_2$. The crystal itself starts to decompose at 170 °C. **1** was characterized by an X-ray single-crystal structure investigation.

From previous structural investigations it was shown that $S(NSO)_2$ has an open-chain structure. The Zn^{2+} ion may be bonded by the sulfur, nitrogen, or oxygen atoms. Furthermore, $S(NSO)_2$ may function as a bidentate chelating or bidentate bridging group. On the basis of vibrational spectroscopy an unambiguous structural assignment could not be made. The S=O and S=N stretching frequencies fall into the same region.

Bond distances and angles are reported in Table III; a view of the structure is shown in Figure 1. The Zn atom, which is located at the inversion center, has an octahedral coordination. It is coordinated by four O atoms from different, but crystallographically related, $S(NSO)_2$ groups and by two F

Table IV. Shortest Contact Distances (Å)

Intermolecular			
S(1)···O(2)	3.109 (2)	S(3)···O(3)	3.188 (3)
S(1)···O(3)	3.167 (3)	S(3)···O(4')	3.21 (1)
S(3)···F(2)	3.065 (2)		

Intramolecular			
S(2)···O(2)	2.985 (2)	S(2)···O(1)	3.110 (2)

atoms from $(AsF_6)^-$ groups. The Zn-O distances of 2.030 (2) and 2.070 (2) Å are in good agreement with similar values in $[Zn(S_3N_2O)_6]^{2+}$.[7]

The Zn-F distance is 2.082 (2) Å. It can be compared with values of 1.97 Å in $ZnPtF_6$,[8] 2.10 Å in $ZnSnF_6$,[9] 2.07 Å in $ZnPdF_6$,[10] and 2.03 Å in $ZnF_2 \cdot 4H_2O$.[11]

The $S(NSO)_2$ groups form chains between the Zn atoms, leading to a two-dimensional network in the $\bar{1}01$ plane.

The S(1)-N(1) and S(3)-N(2) bonds of 1.514 (3) and 1.513 (3) Å correspond to double bonds. The two S-N bonds involving S(2) are slightly shorter than single bonds.

The S-O bonds of 1.468 (2) and 1.475 (2) Å are comparable with the double-bond length in sulfates. The O=S=N—S groups have the cis configuration and do not deviate significantly from planarity.

The entire $S(NSO)_2$ group is rather planar. The largest deviation from planarity is given by S(2) and is 0.067 (1) Å. In the comparison of these values with the structural data of the free ligand[2] it is interesting to note that in **1** all bond distances are longer except the two S-N bonds involving S(2). The O(1)-S(1)-N(1) angle is similar as in the free ligand while the S(1)-N(1)-S(2) and N(1)-S(2)-N(2) angles are slightly enlarged. The crystal packing shows a number of intermolecular interactions that are slightly shorter (up to 0.15 Å) than the sum of the van der Waals radii of the atoms. They are reported in Table IV and are of the type S···O and S···F. In addition the diffuse ring of fluorine atoms approaches the S(1) and S(4) atoms up to 2.9 Å and thus may contribute to the crystal packing in the form of van der Waals contacts.

Supplementary Material Available: Listings of anisotropic temperature factors, observed and calculated structure factor amplitudes, deviations from least-squares planes, and parameters of the fluorine fragments (15 pages). Ordering information is given on any masthead page.

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Biological Analogues. Synthesis of Vicinal Trimercapto Ligands

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The current interest in the synthesis of low molecular weight structural analogues of the protein metal binding sites of, among others, the nitrogenases,[1,2] ferredoxins,[3] metallo-
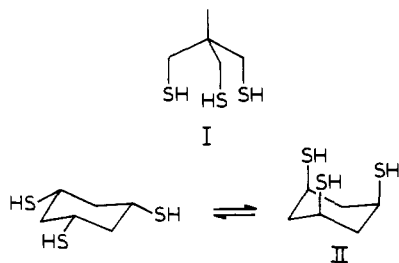
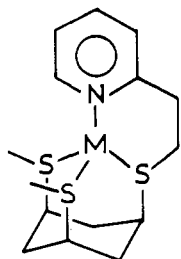**Figure 1.** Structures of the two vicinal trithiol ligands.

Figure 2. Structure of the tetrahedral-enforcing ligand IV.

Figure 3. Synthesis of ligands III and IV.

thioneins,[4] and blue copper proteins[5-8] prompts us to report the facile synthesis of ligands that may have certain desirable characteristics. The two parent ligands are shown in Figure 1; both are vicinal trimercaptide ligands. One of these, I, has its sulfur donor atoms disposed to complex to three cis positions of an octahedron; the other, II, when in the all-axial form, can occupy the cis positions of an octahedron or three positions of a tetrahedron to give an adamantyl structure.

The tritosyl precursors are readily made from the commercially available triol[9] corresponding to I and from *cis*-1,3,5-trihydroxycyclohexane, which is obtained by reduction of phloroglucinol under mild conditions.[10] The introduction of sulfur presents difficulties, which are different for the two cases. The tritosyl precursor of I is a neopentyl system and is very unreactive, and that of II, although somewhat more reactive, is highly prone to elimination if basic sulfur nucleophiles are used. Moreover, high-boiling polar solvents are required for the displacements in both cases. We used the highly nucleophilic but weakly basic isothiocyanate ion to displace the tosyl groups, using the solvents DMF and diethylene glycol for I and II, respectively. Even so, some elimination occurs for the cyclohexyl derivative. Subsequent reduction, with LAH, of the solid triisothiocyanates gave the required trithiols in good yield. Both trithiols are malodorous liquids that are air-sensitive but not inconveniently so. Trithiol I has been prepared before by a long and cumbersome route,[11] and our strategy is similar to the one described for the synthesis of the analogous triamines of I and II.[12]
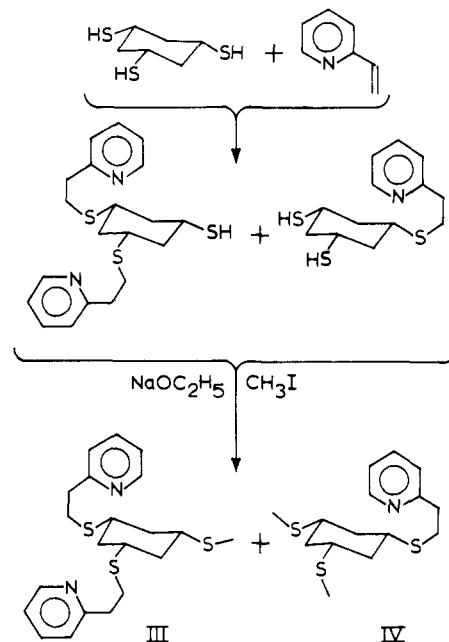
Our interest in these ligands is related to our efforts at stabilizing tetrahedral copper(II) systems containing mercaptide donor atoms. We have so far been unsuccessful in this endeavor with these ligands, but we describe the synthesis of a tetrahedral-enforcing ligand that is of some interest to the blue copper problem. Moreover, the synthetic method we employed, although informal, may be of general applicability. The tetrahedral-demanding quadridentate ligand is shown in Figure 2. It was prepared from II by accepting the statistical outcome of the reaction with 1 molar equiv of 2-vinylpyridine followed by permethylation (Figure 3). This reaction gave roughly equal equivalents of trimethylated II, the disubstituted derivative III, and the desired molecule IV. The trimethylated material[5] was separated from the other two by aqueous acid extraction, and III and IV were easily separated by chromatography.

A methanol solution of [Cu(H$_2$O)$_6$](ClO$_4$)$_2$ when mixed with 1 equiv of IV gives an intensely blue-green species. This solution slowly deposits blue-green crystals at 5 °C, but if the solution is heated or allowed to stand at 25 °C for a few days, white crystals are deposited. These white crystals can also be prepared by allowing [Cu(CH$_3$CN)$_4$]ClO$_4$ to react with IV in acetonitrile solution. The white crystals were analyzed as [Cu(IV)]ClO$_4$; they are diamagnetic and are presumably the tetrahedral copper(I) species of IV. It appears that the [Cu(IV)]$^{2+}$ ion is readily reduced by methanol as might be expected by the presence of the sulfur atoms.[13,14]

The blue-green crystals are a paramagnetic copper(II) complex that, however, is not a tetrahedral monomer. Analytical data suggests a solid polymeric material, and the solution electronic absorption spectrum is consistent with a tetragonal species[5] (d–d at 635 nm (ϵ = 190) and thioether $\rightarrow$ Cu(II) at 410 nm (ϵ = 1600) in acetonitrile–THF (1:4)). We have so far failed to induce IV to form a tetrahedral copper(II) complex either in the solid state or in various solutions. The fact that the trithioether of II forms a copper(II) tetrahedral species in acetic anhydride[5] but IV does not in a

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even at low temperatures, and its copper(I) complex appears to be polymeric.

Experimental Section

1,1,1-Tris(mercaptomethyl)ethane (I).[11] A mixture of 1,1,1-tris-(((tolylsulfonyl)oxy)methyl)ethane[9] (130 g) and KSCN (277 g) in DMF (560 mL) was placed in a 140 °C oil bath and was stirred for 3.75 h. The resulting solution was poured into water (3 L) with stirring. A tan precipitate formed, and after the mixture was allowed to stand at 5 °C for 18 h, the solid was collected and was washed with water, ethanol–ether (1:1), and finally with ether. The air-dried 1,1,1-tris(thiocyanatomethyl)ethane (40.7 g, 75%) was sufficiently pure to be used in the reduction step. It may be recrystallized from hot ethanol (1 g/10 mL) to give an off-white solid, mp 118–120 °C. ^{1}H NMR (CDCl$_3$): δ 1.42 (3 H, s), 3.28 (6 H, s). Anal. Calcd for C$_8$H$_9$N$_3$S$_3$: C, 39.5; H, 3.7; N, 17.3; S, 39.5. Found: C, 39.4; H, 3.6; N, 17.2; S, 39.2.

1,1,1-Tris(thiocyanomethyl)ethane (28.4 g) was added in portions over 1.5 h to a stirred ice-cooled mixture of LAH (13.75 g) in dry ether (300 mL) under N$_2$. The mixture was refluxed for 16 h and then was cooled. The reaction was cautiously quenched by the addition of HCl (6 N, 130 mL) followed by more HCl (12 N, 215 mL). Benzene (200 mL) was then added, and the mixture was stirred for 0.5 h. The organic layer was separated under N$_2$, and the aqueous phase was extracted with benzene (4 × 200 mL) under N$_2$. The combined organic extracts were dried (MgSO$_4$) and then the solvent was removed under reduced pressure. The residue was distilled to give 1,1,1-tris(mercaptomethyl)ethane, a pale yellow oil (13.4 g, 68%; bp 70–72 °C (0.2 mm). ^{1}H NMR (CDCl$_3$): δ 1.00 (3 H, s), 1.30 (3 H, t, J = 8.0 Hz), 2.60 (6 H, d, J = 8.0 Hz). Anal. Calcd for C$_5$H$_{12}$S$_3$: C, 35.7; H, 7.2; S, 57.1. Found: C, 36.0; H, 7.2; S, 57.4.

cis,cis-1,3,5-Trimercaptocyclohexane (II). A mixture of cis,cis-1,3,5-tris((tolylsulfonyl)oxy)cyclohexane[10] (48 g) and KSCN (250 g) in diethylene glycol (200 mL) was heated at 120 °C for 4 h. An amber solution resulted. This was cooled slightly, and water (1250 mL) was added, followed by CH$_2$Cl$_2$–ether (1:1; 200 mL). The layers were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$–ether (1:1; 6 × 100 mL). The combined organic layers were washed with brine (4 × 100 mL) and then were dried over Na$_2$SO$_4$. On removal of the solvents, crude cis,cis-1,3,5-trithiocyanocyclohexane remained as a yellow viscous oil (17.7 g), which slowly crystallized. This was used for the reduction step.

The residue from above was dissolved in dry THF (200 mL) and was added dropwise over 2 h to a suspension of LAH (10 g) in dry THF (450 mL) under N$_2$. After the mixture was stirred at 25 °C for 12 h, the excess of LAH was decomposed by the addition of water (5 mL) followed by 10% aqueous H$_2$SO$_4$ (80 mL). The mixture was filtered, and the solid was washed well with THF. The THF was removed under reduced pressure, to the residue were added water (100 mL) and CH$_2$Cl$_2$ (250 mL), and the layers were separated. The organic layer was washed with water (100 mL) followed by brine (100 mL) and was then dried (Na$_2$SO$_4$); the solvent then was removed under reduced pressure. The residue was distilled to give cis,cis-1,3,5-trimercaptocyclohexane as a pale green viscous oil that solidified at 0 °C (5.6 g, 39%; bp 80–82 °C (0.2 mm). ^{1}H NMR (CDCl$_3$): δ 1.0–1.8 (6 H, m), 2.2–3.1 (6 H, m). Anal. Calcd for C$_6$H$_{12}$S$_3$: C, 40.0; H, 6.7; S, 53.4. Found: C, 40.2; H, 6.8; S, 53.2.

Ligand IV. A solution of cis,cis-1,3,5-trimercaptocyclohexane (5.6 g) and 2-vinylpyridine (3.3 g) in toluene (100 mL) was refluxed under N$_2$ for 5 h. The solvent was removed under reduced pressure, the residue, an amber oil, was dissolved in dry THF (75 mL), and the resulting mixture was added dropwise to an ice-cooled solution of sodium (2.14 g) in absolute ethanol (60 mL) and dry THF (50 mL). A solution of methyl iodide (13.2 g) in dry THF (100 mL) was then added dropwise to the cooled solution. The cooling bath was removed, and the solution was stirred at 25 °C for 3 h. Then, the solvents were removed under reduced pressure, and the residue was slurried with benzene (100 mL) and filtered. In order to extract the pyridine-containing compounds, the benzene filtrate was washed with aqueous HCl (2 N, 6 × 40 mL) and then the combined aqueous extracts were washed with benzene (60 mL). Out of the benzene extracts, the permethylated compound of II may be recovered. The combined acidic aqueous layers were basified with solid NaHCO$_3$ and then were extracted with CH$_2$Cl$_2$ (4 × 70 mL). These combined CH$_2$Cl$_2$ extracts were washed with water (70 mL) and then were dried (Na$_2$SO$_4$). After the solvent was removed, the amber oil (7.0 g) was chromatographed

on alumina (Brockman activity II). Elution with ethyl acetate–benzene (1:25) yielded cis,cis-1-((2-(2-pyridyl)ethyl)thio)-3,5-bis(methylthio)cyclohexane (IV) as a viscous yellow oil (3.2 g, 33%) in the forward fraction; the divinylpyridine compound came off in later fractions. ^{1}H NMR (CD$_3$CN): δ 0.8–1.6 (3 H, m), 2.16 (6 H, s), 2.0–3.1 (6 H, m), 3.02 (4 H, s), 7.0–7.8 (3 H, m), 8.3–8.5 (1 H, m).

[Cu(IV)]ClO$_4$. Ligand IV (0.15 g) was dissolved in dry CH$_3$CN (3 mL), and then solid [Cu(CH$_3$CN)$_4$]ClO$_4$ (0.16 g) was added. When all of the solid had dissolved, methanol (10 mL) was added, and the volume was reduced on a steam bath to ~10 mL. The solution was slowly cooled to 25 °C and then was kept at 5 °C for 18 h. The white precipitate was then filtered, washed with methanol containing a few drops of CH$_3$CN, and vacuum dried, yielding a fine white solid (0.14 g, 59%). ^{1}H NMR (CD$_3$CN): δ 0.19–1.7 (3 H, m), 2.0–3.1 (6 H, m), 2.16 (6 H, s), 3.12 (4 H, s), 7.2–8.0 (3 H, m), 8.3–8.5 (1 H, m). Anal. Calcd for [Cu(C$_{15}$H$_{23}$NS$_3$)]ClO$_4$: C, 37.8; H, 4.9; N, 2.9; S, 20.2; Cl, 7.4. Found: C, 37.7; H, 4.9; N, 3.2; S, 20.1; Cl, 7.5.

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Second Dissociation Constant of Hydrogen Sulfide

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Published values for the pK_{a2} values of hydrogen sulfide cover a range of almost 8 orders of magnitude.[2] Most of the 22 values quoted by Sillén[3] are larger than K_w. Two contradictory values have been published in an earlier volume of this journal: Stephens[4] selected a value of pK_{a2} = 13.78 ± 1.0 based on calorimetric and thermodynamic reasoning, and Giggenbach[5] derived a value of pK_{a2} = 17.1 ± 0.2 from an UV study that involved reassigned absorption bands. Recent reviews[6] by CODATA[2] and Rao[7] prefer values below pK_w.

In this study we used a Raman spectrometric method[8,9] for in situ identification of the H–S stretch in high-pH solutions and for estimating their concentrations.

Experimental Section

Samples were prepared on a vacuum line in 10-mm diameter Pyrex ampules. The ampules were charged with 1 mL of sodium hydroxide solution prepared by dissolving reagent grade sodium hydroxide pellets in doubly distilled water under nitrogen gas. The sodium hydroxide concentration was determined by weighing and by titration of the solution after the experiments were completed. Sulfide was determined gravimetrically after oxidation and precipitation as barium sulfate. Sodium hydroxide concentrations ranged from 5 to 22 N. Hydrogen sulfide was kept between 0.3 and 0.6 M. All solutions also contained 0.10 M NaClO$_4$ for use as an internal Raman scattering standard.[10] The samples were frozen at 76 K, and a measured amount of hydrogen sulfide gas was condensed in the ampules to yield the desired con-

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