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Copper(I) Complexes of 14- and 16-Membered Chelating Macrocycles with Trans-Disposed Pairs of Imine-*N* and Thioether-*S* Donors: Crystal and Molecular Structures of $[Cu(C_{18}H_{18}N_2S_2)]CF_3SO_3$ and $[Cu(C_{20}H_{22}N_2S_2)]CF_3SO_3$

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Barium manganate oxidation of 2-((2-aminoethyl)thio)benzenemethanol (**1**) produces a high yield of the unsaturated 14-membered *trans*-N_2S_2 quadridentate 6,7,15,16-tetrahydrodibenzo[*f*,*m*][1,8,4,11]dithiadiazacyclotetradecine (**3**); oxidation of the corresponding 2-((3-aminopropyl)thio) compound **2** produces 16-membered 7,8,16,17,18-pentahydro-1*H*,6*H*-dibenzo[*g*,*o*][1,9,5,13]-dithiadiazacyclohexadecine (**4**). Diimine **3** undergoes a quantitative acid-catalyzed rearrangement in solution into the seven-membered 2,3-dihydro-1,4-benzothiazepine (**5**); **4** rearranges into 3,4-dihydro-2*H*-1,5-benzothiazocine (**6**). Monomers **5** and **6** spontaneously dimerize upon removal of solvent but are trapped as the corresponding amines **9** and **10** by reduction with $LiAlH_4$. Reduction of **3** and **4** produces the macrocyclic diamines **7** and **8**, respectively. The diimines readily complex copper(I) and copper(II), giving air-stable triflate salts. Indeed, deep orange $[Cu(\mathbf{4})]CF_3SO_3$ was recrystallized from hot water without decomposition. The crystal structures of $[Cu(\mathbf{3})]CF_3SO_3$ and $[Cu(\mathbf{4})]CF_3SO_3$ at 21 ± 1 °C have been determined. For $[Cu(C_{18}H_{18}N_2S_2)]CF_3SO_3$ (**11**): space group $P\bar{1}$, a = 13.003 (1) Å, b = 19.353 (1) Å, c = 8.478 (1) Å, α = 86.25 (1)°, β = 88.91 (1)°, γ = 67.25 (1)°, Z = 2, R = 0.030, R_w = 0.052. For $[Cu(C_{20}H_{22}N_2S_2)]CF_3SO_3$ (**12**): space group $P2_1/c$, a = 13.297 (1) Å, b = 10.437 (1) Å, c = 17.464 (1) Å, β = 100.11 (1)°, Z = 4, R = 0.030, R_w = 0.043. Both complexes have distorted tetrahedral structures with longer Cu–S bond distances in the complex of 16-membered **4**. The most significant deviations from tetrahedral coordination of the copper(I) ions are the large S–Cu–S bond angles: 152.17 (3)° in the complex of **3**; 132.07 (3)° in the complex of **4**. Both cations form stable adducts with triphenylphosphine.

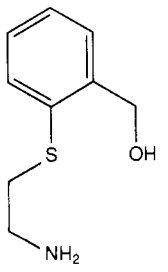
Introduction

There is an intense interest in copper enzymes involved in electron-transfer processes.[2,3] The active sites of these proteins exhibit anomalous spectroscopic and redox properties, with rates of electron transfer being dependent upon the nature of the ligands and the stereochemical requirements they impose upon the metal ions.[4,5] The blue copper (type I) enzymes, in particular, plastocyanin and azurin, contain single copper ions with distorted tetrahedral geometries at their active sites. In each case, two imidazole N atoms of two histidine residues, a thiolato S atom of a cysteine residue, and a thioether S atom of a methionine residue provide the four donors to the copper center. As a consequence, copper(I) and copper(II) complexes of mixed N- and S-donor ligands have been investigated as models for understanding the more complicated stereo- and electrochemical behavior of the related enzymes[6–8] although the data are biased toward the spectroscopically rich copper(II) halves of the redox couples.

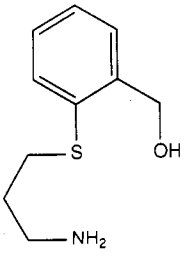
In recent work, we discovered a convenient synthesis of the 14-membered *trans*-N_2S_2 macrocycle **3**.[9] We now find that 16-membered **4** can be prepared by a similar route and that both it and **3** form deeply colored air-stable crystalline derivatives of copper(I) triflate.

Results and Discussion

Barium manganate oxidations of 2-((2-aminoethyl)thio)-benzenemethanol (**1**) or of the corresponding 2-((3-amino-propyl)thio) compound (**2**) in dichloromethane over ca. 16 h at



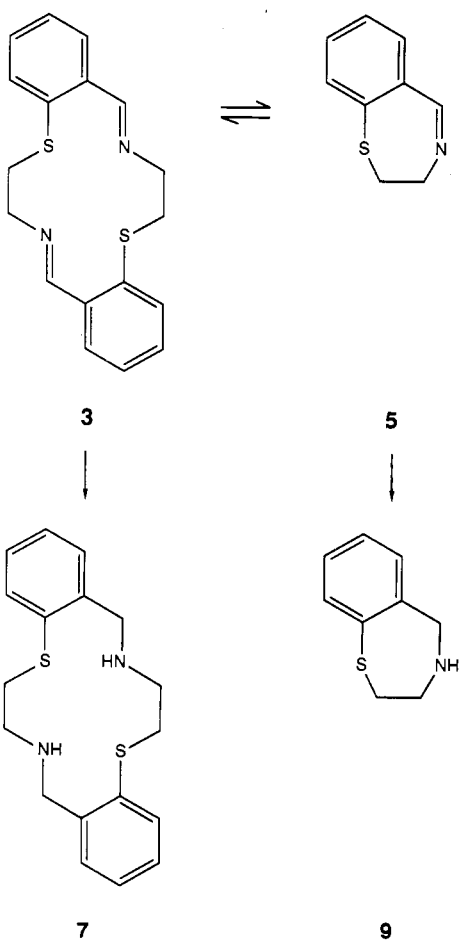
1



2

20 °C produces 85–90% yields of the macrocyclic *trans*-N_2S_2 quadridentates 6,7,15,16-tetrahydrodibenzo[*f*,*m*][1,8,4,11]dithiadiazacyclotetradecine (**3**) and 7,8,16,17,18-pentahydro-1*H*,6*H*-dibenzo[*g*,*o*][1,9,5,13]dithiadiazacyclohexadecine (**4**), respectively (Chart I and Schemes I and II).[10]

Scheme I



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(1) Present address: School of Physical Sciences, Flinders University of South Australia, Bedford Park, South Australia 5042, Australia.
(2) Ryden, L.; Lundgren, J.-O. *Nature (London)* **1976**, *261*, 344 and references cited therein.
(3) Freeman, H. C. In *Coordination Chemistry*; Laurent, J. P., Ed.; Pergamon: New York, 1980; Vol. 21, p 29.

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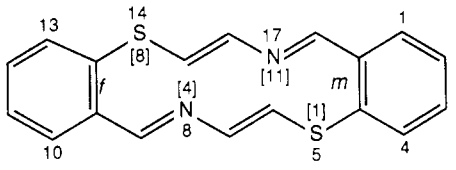
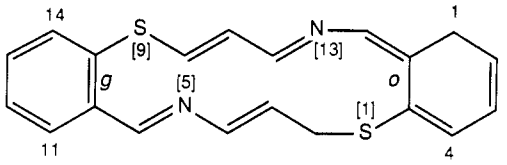
Chart I. Parent Ring System for Systematic Names[10]

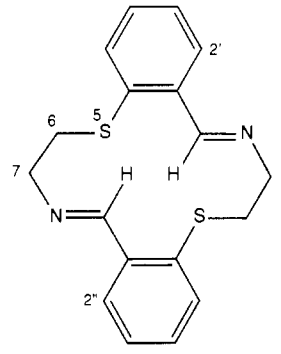


Dibenzo[f,m][1,8,4,11]dithiadiazacyclotetradecine



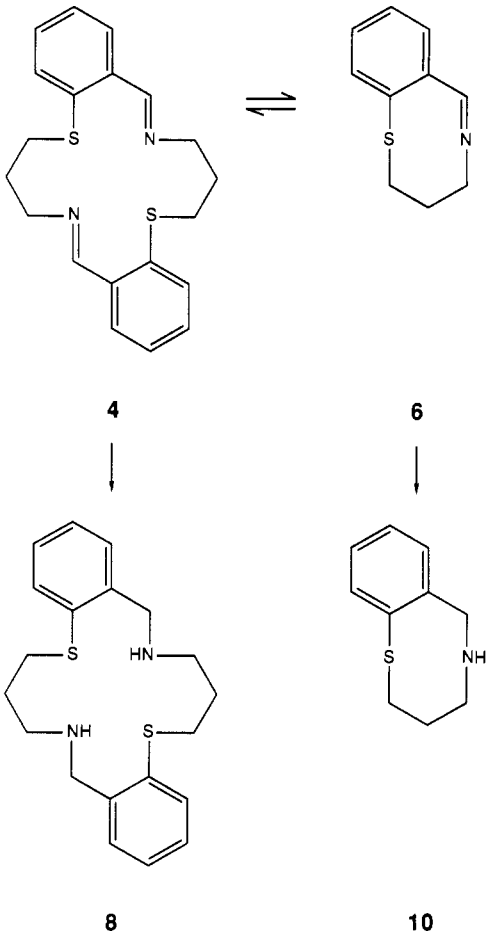
1H,6H-Dibenzo[g,o][1,9,5,13]dithiadiazacyclohexadecine

The spontaneous double condensations take place without regard to concentration or any of the other precautions usually taken to avoid polymerization, such as the use of a metal template. Treatment of the crude reaction products with $[Ni(H_2O)_6]Cl_2$ yielded the green complexes *cis*-$[NiCl_2(\mathbf{3})]$[11] and *cis*-$[NiCl_2(\mathbf{4})]$ from which the pure ligands were isolated by displacement with ammonia in 85–90% yields as colorless crystals. The dimeric structures of the free ligands were confirmed by molecular weight determinations in dichloromethane. The nonchelating trans-trans-endo conformation was assigned to 14-membered **3** on the basis of the strong deshielding of the azomethine proton (δ 8.83) and of the aromatic protons $H_{2'}$ and $H_{2''}$ (δ 8.06). In the 4,5-dihydro-3*H*-2-benzazepine dimer of similar structure the azomethine proton resonance occurs at 8.46 ppm.[12] Syntheses of *trans*-N_2S_2 macrocyclic quadridentates of this type have not been available hitherto, although the corresponding cis isomer of **3** was prepared by Busch and Lindoy in 1969.[13]

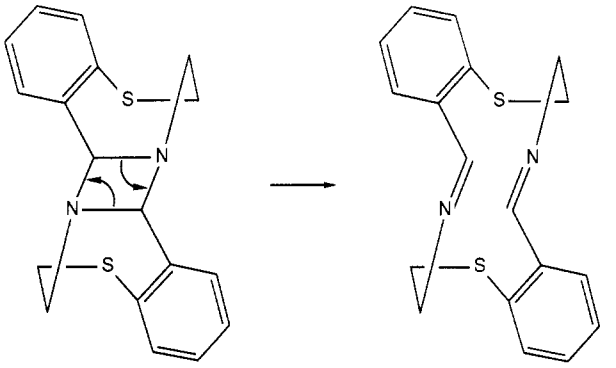


trans,trans,endo-**3**

Scheme II



Scheme III



Dimer–Monomer Interconversions. Diimines **3** and **4** undergo facile conversions into 2,3-dihydro-1,4-benzothiazepine (**5**) and 3,4-dihydro-2*H*-1,5-benzothiazocine (**6**) respectively (Chart I and Schemes I and II). The conversions occur slowly ($t_{1/2}$ ca. 8 h) in chloroform but are accelerated by trifluoroacetic acid. The reactions were monitored by ^1H NMR spectroscopy (low-field

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(10) *Chemical Abstracts 10th Collective Index Guide 1977–1981*, for Vols. 86–95; American Chemical Society: Washington, DC, 1981; Appendix IX. *Chemical Abstracts Ring Systems Handbook, Ring System File, 1984 Edition*; American Chemical Society: Washington, DC, 1984.
(11) A preliminary account of the crystal and molecular structure of *cis*-$[NiCl_2(\mathbf{3})]$ has been published;[9] the paramagnetic triclinic crystals (μ_{eff} = 3.23 μ_B at 20 °C) each contain two conformers of the octahedral complex.
(12) Goldman, I. M.; Larson, J. K.; Tretter, J. R.; Andrews, E. G. *J. Am. Chem. Soc.* **1969**, *91*, 4941.
(13) Lindoy, L. F.; Busch, D. H. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 525.

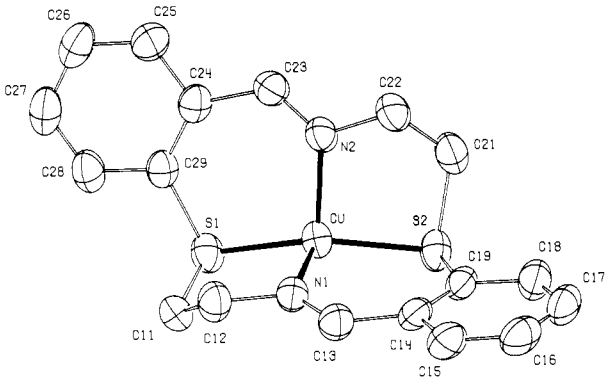

Figure 1. View of the $[Cu(C_{18}H_{18}N_2S_2)]^+$ cation in **11**, showing the atom-labeling scheme of the non-hydrogen atoms. Thermal ellipsoids enclose 50% probability levels (hydrogen atoms have been omitted for clarity).

azomethine resonances are replaced by azomethine resonances at δ 8.53 for the monomer of **3**, and at δ 8.94 for the monomer of **4**) and by osmometry. Unlike 1,3-dihydro-1,4-benzoxazepine, which can be isolated by distillation,[14] benzothiazepine **5** and benzothiazocine **6** dimerize upon removal of solvent.

Although other pathways may be available, the present data suggest that the facile interconversions are acid-catalyzed. The observation of complete monomerization of **3** and **4** in acidic chloroform solution and the dimerization of neat **5** and of neat **6** suggest comparable stabilities for the monomers and dimers. As suggested for the acid-catalyzed interconversions of 4,5-dihydro-3*H*-2-benzazepine and its dimer,[13] a stepwise scheme involving a 1,3-diazetidine intermediate is envisaged for the interconversions between **3** and **5** (Scheme III) and between **4** and **6**. Although there was no evidence of diazetidine formation in the present work, Schiff base dimerizations to 1,3-diazetidines and Schiff base exchange reactions via diazetidines have been reported.[15] Other work in our laboratory supports the hypotheses of 1,3-diazetidine intermediates: (±)-1,3-dihydro-1-methyl-4,1-benzazarsepine dimerizes *stereospecifically* into (9*R**,18*S**)-7,8,9,16,17,18-hexahydro-9,18-dimethyldibenzo[*e*,*l*][1,8,4,11]-diazadiarsacyclotetradecine.[16]

Saturated *trans*-N_2S_2 Macrocycles. The addition of **3** or **4** as solids to suspensions of $LiAlH_4$ in tetrahydrofuran led to almost quantitative yields of crystalline diamines **7** and **8**. On the other hand, treatment of the diimines with a trace of TFA (in boiling diethyl ether) prior to reduction gave the respective monoamines (**9** and **10**), which were isolated by distillation as colorless liquids (Schemes I and II). The corresponding 14- and 16-membered *cis*-N_2S_2 macrocycles are known.[17]

Copper(I) Triflates of Diimines 3 and 4. Dichloromethane solutions of $[Cu(MeCN)_4]CF_3SO_3 \cdot 0.5H_2O$[18] turned bright red when **3** or **4** were added. Dilution of the solutions with diethyl ether yielded the air-stable orange products $[Cu(\mathbf{3})]CF_3SO_3$ (**11**) and $[Cu(\mathbf{4})]CF_3SO_3$ (**12**). Both compounds conducted as univalent electrolytes in methanol solutions, and both were recovered from the respective solutions by dilution with diethyl ether. The complexes are remarkably stable to atmospheric oxidation and to hydrolysis. Indeed, $[Cu(\mathbf{2})]CF_3SO_3$ was recrystallized from hot water without decomposition. In contrast, attempted preparations of the related copper(I) complexes derived from diamines **7** and **8** were unsuccessful, leading to intractable paramagnetic products, even when the reactions were carried out under rigorously anhydrous and anaerobic conditions. This observation clearly indicates the significant role that the π-acceptor imino group can play in stabilizing copper(I).

Table I. Crystal Parameters and Experimental Data for X-ray Diffraction Measurements on $[Cu(C_{18}H_{18}N_2S_2)](CF_3SO_3)$ (**11**) and $[Cu(C_{20}H_{22}N_2S_2)](CF_3SO_3)$ (**12**)[a]

	11	**12**
empirical formula	$C_{19}H_{18}CuF_3N_2O_3S_3$	$C_{21}H_{22}CuF_3N_2O_3S_3$
fw	539.08	567.14
lattice type	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
cell dimens		
a, Å	13.003 (1)	13.297 (1)
b, Å	10.353 (1)	10.437 (1)
c, Å	8.478 (1)	17.464 (1)
α, deg	86.25 (1)	90.0
β, deg	88.91 (1)	100.11 (1)
γ, deg	67.25 (1)	90.0
V, Å^3	1050.28	2386.03
Z	2	4
ρ_{calcd}, g cm^{-3}	1.704	1.579
cryst size, mm	0.20 × 0.35 × 0.18	0.06 × 0.19 × 0.23
μ(Cu Kα), cm^{-1}	46.7	41.4
data collcn instrum	Picker FACS-I	Picker FACS-I
radiation (graphite monochromated)	Cu Kα	Cu Kα
λ(radiation), Å	1.5405 (α_1)	1.5405 (α_1)
orientation reflcns: no.; range (2θ), deg	12; 95–118	12; 99–114
temp, °C	21 ± 1	21 ± 1
scan method	θ–2θ	θ–2θ
scan range (2θ), deg	3–120	3–120
no. of unique data; total with $F_o^2 > 3\sigma(F_o^2)$	3136; 3002	3546; 3046
no. of params refined	281	308
R[b]	0.030	0.030
R_w[c]	0.052	0.043
quality-of-fit indicator[d]	2.96	1.78
largest shift/esd, final cycle	0.03	0.03
largest peak, e Å^{-3}	0.44	0.28

[a] The estimated standard deviation in the least significant digit is shown in parentheses for each entry in this and subsequent tables. [b] $R_w = \sum||F_o| - |F_c||/|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [d] Quality of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

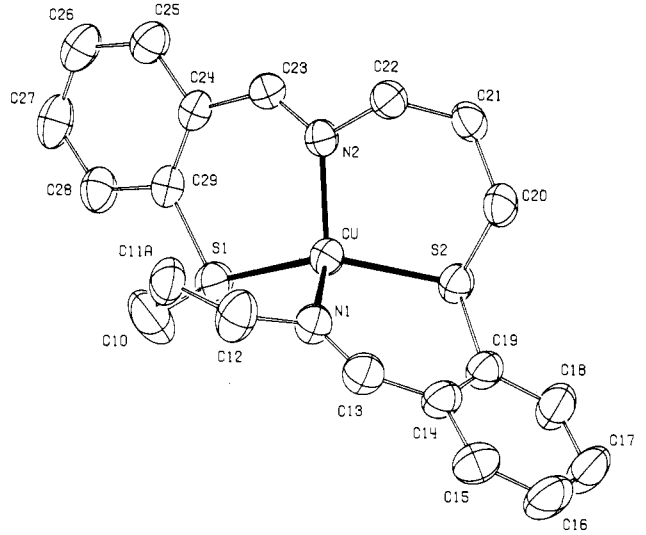

Figure 2. $[Cu(C_{20}H_{22}N_2S_2)]^+$ cation in **12**. Only one position of disordered atom C(11) is shown. Thermal ellipsoids enclose 50% probability levels (hydrogen atoms have been omitted for clarity).

Crystal and Molecular Structures of $[Cu(\mathbf{3})]CF_3SO_3$ (11) and $[Cu(\mathbf{4})]CF_3SO_3$ (12). Crystal data for the two complexes are given in Table I. Tables II and III give the positional parameters, and Table IV lists the most important distances and angles in the two compounds. Complete data are available in the supplementary material.

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(17) Lindoy, L. F.; Smith, R. J. *Inorg. Chem.* **1981**, *20*, 1314.
(18) This compound was prepared by a method similar to that used for the preparation of the corresponding hexafluorophosphate salt.[19]
(19) Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90.

Table II. Atomic Positional Parameters for Non-Hydrogen Atoms in $[Cu(C_{18}H_{18}N_2S_2)](CF_3SO_3)$ (**11**)

atom	x	y	z
Cu	0.24751 (3)	0.49938 (3)	0.07772 (4)
S(1)	0.19490 (5)	0.32671 (6)	0.02904 (7)
C(11)	0.3123 (2)	0.1915 (3)	0.1351 (3)
C(12)	0.3597 (2)	0.2450 (3)	0.2686 (3)
N(1)	0.3714 (2)	0.3762 (2)	0.2184 (2)
C(13)	0.4542 (2)	0.4003 (3)	0.2614 (3)
C(14)	0.4730 (2)	0.5317 (3)	0.2324 (3)
C(15)	0.5631 (2)	0.5339 (3)	0.3187 (3)
C(16)	0.5916 (2)	0.6501 (3)	0.3126 (4)
C(17)	0.5318 (2)	0.7663 (3)	0.2185 (3)
C(18)	0.4443 (2)	0.7658 (3)	0.1269 (3)
C(19)	0.4135 (2)	0.6517 (2)	0.1343 (3)
S(2)	0.30113 (5)	0.67206 (3)	0.00090 (7)
C(21)	0.1819 (2)	0.8070 (3)	0.0902 (3)
C(22)	0.1340 (2)	0.7534 (3)	0.2327 (3)
N(2)	0.1218 (2)	0.6231 (2)	0.2020 (2)
C(23)	0.0381 (2)	0.6002 (3)	0.2521 (3)
C(24)	0.0186 (2)	0.4699 (2)	0.2420 (3)
C(25)	−0.0739 (2)	0.4685 (3)	0.3293 (3)
C(26)	−0.1033 (2)	0.3545 (3)	0.3407 (3)
C(27)	−0.0416 (2)	0.2360 (3)	0.2624 (4)
C(28)	0.0481 (2)	0.2352 (3)	0.1707 (3)
C(29)	0.0802 (2)	0.3490 (2)	0.1613 (3)
S(3)	0.24468 (5)	0.05503 (6)	0.70821 (7)
O(1)	0.3466 (2)	−0.0117 (2)	0.7949 (3)
O(2)	0.2281 (2)	0.1893 (2)	0.6314 (2)
O(3)	0.1493 (2)	0.0459 (2)	0.7875 (3)
C(1)	0.2616 (3)	−0.0525 (3)	0.5440 (3)
F(1)	0.2777 (2)	−0.1849 (2)	0.5893 (2)
F(2)	0.3509 (3)	−0.0595 (3)	0.4612 (3)
F(3)	0.1786 (3)	−0.0067 (2)	0.4479 (3)

Table III. Atomic Positional Parameters for Non-Hydrogen Atoms in $[Cu(C_{20}H_{22}N_2S_2)](CF_3SO_3)$ (**12**)

atom	x	y	z
Cu	0.68418 (3)	0.89261 (4)	0.45649 (2)
S(1)	0.68168 (5)	0.98038 (7)	0.33871 (4)
C(10)	0.7600 (3)	0.8632 (5)	0.2992 (2)
C(11A)[a]	0.7512 (4)	0.7373 (5)	0.3253 (3)
C(11B)[b]	0.8425 (6)	0.7837 (9)	0.3382 (5)
C(12)	0.8161 (2)	0.6959 (3)	0.4046 (2)
N(1)	0.8074 (2)	0.7812 (2)	0.4698 (1)
C(13)	0.8798 (2)	0.7763 (3)	0.5277 (2)
C(14)	0.8974 (2)	0.8550 (3)	0.5986 (2)
C(15)	0.9923 (2)	0.8364 (3)	0.6459 (2)
C(16)	1.0241 (3)	0.9043 (4)	0.7131 (2)
C(17)	0.9615 (3)	0.9974 (4)	0.7347 (2)
C(18)	0.8665 (2)	1.0184 (3)	0.6894 (2)
C(19)	0.8327 (2)	0.9482 (3)	0.6228 (2)
S(2)	0.70451 (5)	0.97823 (6)	0.57618 (4)
C(20)	0.6400 (2)	0.8535 (3)	0.6228 (1)
C(21)	0.5319 (2)	0.8285 (3)	0.5807 (2)
C(22)	0.5226 (2)	0.7407 (2)	0.5098 (2)
N(2)	0.5485 (1)	0.8087 (2)	0.4417 (1)
C(23)	0.4806 (2)	0.8087 (2)	0.3806 (1)
C(24)	0.4824 (2)	0.8702 (2)	0.3051 (1)
C(25)	0.3923 (2)	0.8524 (3)	0.2512 (2)
C(26)	0.3778 (2)	0.9048 (3)	0.1775 (2)
C(27)	0.4530 (3)	0.9789 (3)	0.1556 (2)
C(28)	0.5431 (2)	0.9985 (3)	0.2074 (2)
C(29)	0.5599 (2)	0.9454 (2)	0.2814 (1)
S(3)	0.22711 (5)	0.93701 (7)	0.91432 (4)
O(1)	0.2538 (2)	0.8532 (2)	0.8558 (1)
O(2)	0.1556 (2)	1.0339 (3)	0.8847 (2)
O(3)	0.3092 (2)	0.9801 (2)	0.9719 (1)
C(1)	0.1581 (3)	0.8319 (5)	0.9685 (3)
F(1)	0.1224 (2)	0.8929 (3)	1.0240 (2)
F(2)	0.0822 (2)	0.7744 (3)	0.9236 (2)
F(3)	0.2192 (3)	0.7396 (3)	1.0039 (2)

[a] Occupancy 0.65. [b] Occupancy 0.35.

The coordination geometry of the copper(I) ion in each of the complex cations is distorted tetrahedral with N(1)–Cu–N(2) = 110.88 (8)° in **11** and 118.00 (9)° in **12**; S(1)–Cu–S(2) = 152.17 (3)° in **11** and 132.07 (3)° in **12** (Figures 1 and 2). The cations in each case are dissymmetric (C_2 symmetry), although the crystals themselves are achiral racemic compounds. Although copper–sulfur bond lengths appear to be particularly sensitive to stereoelectronic factors within the complexes, the macrocyclic thioether-*S*–Cu(I) bond lengths in **11** [2.212 (6) Å, average] and **12** [2.246 (6) Å, average] correspond closely in value to those in similar complexes where the thioether-*S* donors approach trans coordination.[8] The slight lengthening of Cu–S bonds in the complex of the larger ringed ligand is also consistent with other work.[20] Caution is required, however, in generalizing about factors influencing bond lengths in these systems: the thiolato-*S*–Cu(II) and the imine-*N*–Cu(II) bond lengths in a pseudotetrahedral complex of a sterically constrained linear quadridentate ligand are almost identical with those found in **12**.[7]

Table IV. Important Bond Distances (Å) and Angles (deg) in **11** and **12**

	11	**12**
Cu–N(1)	1.982 (2)	1.989 (2)
Cu–N(2)	1.978 (2)	1.981 (2)
Cu–S(1)	2.211 (1)	2.247 (1)
Cu–S(2)	2.214 (1)	2.246 (1)
N(1)–Cu–N(2)	110.88 (8)	118.00 (9)
S(1)–Cu–S(2)	152.17 (3)	132.07 (3)
N(1)–Cu–S(1)	92.93 (6)	103.00 (7)
N(1)–Cu–S(2)	102.83 (6)	99.31 (6)
N(2)–Cu–S(1)	102.87 (6)	101.21 (6)
N(2)–Cu–S(2)	92.85 (6)	104.77 (6)

Triphenylphosphine Adducts. Both $[Cu(\mathbf{3})]CF_3SO_3$ and $[Cu(\mathbf{4})]CF_3SO_3$ form air-stable crystalline adducts with triphenylphosphine, viz. $[Cu(\mathbf{3})PPh_3]CF_3SO_3$ (**13**) and $[Cu(\mathbf{4})PPh_3]CF_3SO_3$(**14**), respectively. The adducts are orange-yellow in color and both conduct as uni-univalent electrolytes in dichloromethane, which apparently indicates five-coordination of the copper(I) ions in both cases, although the physical data available do not rule out structures of lower coordination number in which the phosphine has substituted one or more of the macrocyclic ligand donors in the four-coordinate starting materials. An X-ray crystal structure determination of $[Cu(\mathbf{3})PPh_3]CF_3SO_3$ is in progress. Attempted adduct formation with carbon monoxide, dioxygen, or imidazole led to no observable reaction.

Diimines **3** and **4** and diamines **7** and **8** react with copper(II) triflate in methanol to give blue-black solutions of the corresponding copper(II) complexes. X-ray crystal structure determinations of the complexes are in progress. Full details of the structures, along with a description of their spectroscopic and electrochemical properties, will be reported separately.

Experimental Section

Proton NMR spectra were recorded at 20 °C with use of a Jeolco FX-200 spectrometer: chemical shifts are quoted as δ values relative to internal Me_4Si. Molar conductivities were measured with a Wissenschaftlich-Technische Werkstatten (D-8120 Weilheim, FRG) conductivity bridge for 10^{-3} M solutions at 20 °C. Elemental analyses were performed by staff within the Research School of Chemistry. The preparation of 2-mercaptobenzenemethanol is an improvement on the literature method.[21]

Ligand Syntheses. 2-Mercaptobenzenemethanol. A solution of 2-mercaptobenzoic acid (60 g, 0.39 mol) in tetrahydrofuran (250 mL) was added over 1 h into a suspension of $LiAlH_4$ (25 g, 0.66 mol) in the same solvent (1 L) at 0 °C. The mixture was then heated under reflux for 30 min and cooled (to ca. 0 °C) and excess $LiAlH_4$ decomposed by the addition of a saturated solution of sodium sulfate in H_2SO_4 (75 mL, 18 M). After 1 h at ca 20 °C the gray precipitate was filtered from the reaction mixture and washed with dichloromethane (3 × 300 mL). Evaporation to dryness of the filtrate and the washings yielded the

(20) Pett, V. B.; Diaddario, L. L.; Dockal, E. R.; Corfield, P. W.; Ceccarelli, C.; Glicks, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1983**, *22*, 3661.
(21) Grice, R.; Owen, L. N. *J. Chem. Soc.* **1963**, 1947.

product as an orange liquid; yield 45 g (82%). Colorless crystals of the pure compound were obtained by distillation; bp 85 °C (0.03 mmHg) (lit.[21] bp 85 °C (0.001 mmHg)). ^{1}H NMR ($CDCl_3$): δ 7.40–7.00 (m, 4 H, Ar*H*), 4.76 (s, 2 H, CH_2O). IR (Nujol): 3350 (ν_{OH}), 2585 cm^{-1} (ν_{SH}).

The crude product was used in the subsequent step. (Attempted large-scale purification by distillation often resulted in the formation of an uncharacterizable solid.)

2-((2-Aminoethyl)thio)benzenemethanol (1). A solution of NaOH (18.4 g, 0.46 mol) in ethanol (250 mL) was added slowly to a solution of the mercaptan (25 g, 0.18 mol) and 2-chloroethanamine hydrochloride (32 g, 0.27 mol) in methanol (300 mL) at room temperature. The mixture was stirred overnight and filtered, and the filtrate was concentrated. Water was added to the concentrate, and the product was extracted into dichloromethane (3 × 250 mL). Evaporation of the dried ($MgSO_4$) extracts yielded an orange oil from which colorless needles of the pure compound were obtained by crystallization from ethanol–dichloromethane mixture: yield 23 g (70%), mp 72–75 °C. Anal. Calcd for $C_9H_{13}NOS$: C, 59.0; H, 7.2; N, 7.6; S, 17.5. Found: C, 59.2; H, 7.3; N, 7.7; S, 17.2. ^{1}H NMR ($CDCl_3$): δ 7.42–7.20 (m, 4 H, Ar*H*), 4.74 (s, 2 H, CH_2O), 2.98 (t, 2 H, ^3J = 6.3 Hz, CH_2N), 2.81 (t, 2 H, ^3J = 6.3 Hz, CH_2S), 2.74 (s, 3 H, NH_2,OH). ^{13}C NMR ($CDCl_3$): δ 142.7–127.4 (Ar*C*), 63.4 (CH_2O), 40.5 (CH_2N), 38.3 (CH_2S). IR (Nujol): 3340, 3280 cm^{-1} (ν_{OH}, ν_{NH}). Mass spectrum: *m/e* 183 [M]$^+$.

2-((3-Aminopropyl)thio)benzenemethanol (2). This compound was prepared from 2-mercaptobenzenemethanol (25 g, 0.18 mol) and 3-chloropropanamine hydrochloride (35 g, 0.27 mol) by a method similar to that described for the ethyl homologue; yield 28 g (80%). An analytically pure sample was obtained as a viscous pale yellow liquid by distillation of the crude product; bp 170 °C (0.05 mmHg). Anal. Calcd for $C_{10}H_{15}NOS$: C, 60.9; H, 7.7; N, 7.1. Found: C, 60.5; H, 7.7; N, 7.2. ^{1}H NMR ($CDCl_3$): δ 7.43–7.21 (m, 4 H, Ar*H*), 4.77 (s, 2 H, CH_2O), 2.99 (t, 2 H, ^3J = 7.1 Hz, CH_2N), 2.83 (t, 2 H, ^3J = 7.1 Hz, CH_2S), 2.04 (s, 3 H, NH_2, OH), 1.77 (q, 2 H, ^3J = 7.1 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ 140.8–125.4 (Ar*C*), 61.1 (CH_2O), 40.0 (CH_2N), 31.5 (CH_2S), 30.3 (CH_2). IR (Nujol): 3340, 3270 cm^{-1} (ν_{OH}, ν_{NH}). Mass spectrum: *m/e* 197 [M]$^+$. The crude product was used in the subsequent conversion into macrocycle without apparent loss of the yield.

6,7,15,16-Tetrahydrodibenzo[*f*,*m*][1,8,4,11]dithiadiazacyclotetradecine (3). A solution of 2-((2-aminoethyl)thio)benzenemethanol (20 g, 0.11 mol) in dichloromethane (1.2 L) was stirred for ca 12 h with $BaMnO_4$ (140 g, excess) at room temperature. The reaction mixture was then filtered, and the filtrate was taken to dryness. The glassy product was redissolved in dichloromethane (100 mL), and the solution was treated with $[Ni(H_2O)_6]Cl_2$ (14 g, 0.06 mol) in methanol (150 mL). The reaction mixture was heated on the steam bath for ca. 30 min and cooled to room temperature prior to filtering off the bright green nickel(II) complex. Additional complex was obtained from the concentrated filtrate. Total yield: 22.4 g (90%). The green nickel(II) complex was suspended in methanol (100 mL), and concentrated aqueous ammonia (500 mL) was added to the mixture. A white crystalline precipitate separated during overnight stirring of the mixture; it was washed with concentrated ammonia (200 mL) and water (3 × 200 mL), and then it was dried at 40 °C (in vacuo). The pure product was thus obtained as fine crystalline needles in 15.2 g (95%) yield; mp 206–209 °C dec. Anal. Calcd for $C_{18}H_{18}N_2S_2$: C, 66.2; H, 5.6; N, 8.6. Found: C, 66.2; H, 5.7; N, 8.6. ^{1}H NMR ($CDCl_3$): δ 8.83 (s, 2 H, CH=N), 8.06 (dd, 2 H, ^3J = 7.8 Hz, ^4J = 1.7 Hz, Ar–2H), 7.66–7.27 (m, 6 H, Ar*H*), 3.60 (t, 4 H, ^3J = 5.0 Hz, CH_2N), 3.38 (t, 4 H, ^3J = 5.0 Hz, CH_2S). ^{13}C NMR ($CDCl_3$): δ 162.9 (CH=N), 139.3–127.4 (Ar*C*), 59.3 (CH_2N), 39.1 (CH_2S). IR (Nujol): 1640 cm^{-1} ($\nu_{C=N}$). Mass spectrum: *m/e* 326 [M]$^+$. Mol wt (osmometry, CH_2Cl_2): 326 (calcd); 324 (found).

7,8,16,17,18-Pentahydro-1*H*,6*H*-dibenzo[*g*,*o*][1,9,5,13]dithiadiazacyclohexadecine (4). This compound was prepared from 2-((3-aminopropyl)thio)benzenemethanol in 90% yield by a method similar to that used for **3**; mp 120–122 °C. Anal. Calcd for $C_{20}H_{22}N_2S_2$: C, 67.8; H, 6.3; N, 7.9. Found: C, 67.3; H, 6.4; N, 8.1. ^{1}H NMR ($CDCl_3$): δ 9.01 (s, 2 H, CH=N), 7.92–7.25 (m, 8 H, Ar*H*), 3.82 (t, 4 H, ^3J = 6.6 Hz, CH_2N), 2.85 (t, 4 H, ^3J = 6.6 Hz, CH_2S), 2.02 (q, 4 H, ^3J = 6.6 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ 161.6 (CH=N), 138.1–128.3 (Ar*C*), 60.3 (CH_2N), 36.0 (CH_2S), 29.6 (CH_2). IR (Nujol): 1640 cm^{-1} ($\nu_{C=N}$). Mass spectrum: *m/e* 354 [M]$^+$. Mol wt (osmometry, CH_2Cl_2): 354 (calcd), 345 (found).

2,3-Dihydro-1,4-benzothiazepine (5). To a solution of **3** (1 g, 3 mmol) in dichloromethane (50 mL) was added trifluoroacetic acid (0.1 mL) at room temperature (ca 20 °C). After ca 12 h the ^{1}H NMR spectrum of the solution indicated mainly monomeric product. ^{1}H NMR ($CDCl_3$): δ 8.53 (s, 1 H, CH=N), 7.49–7.29 (m, 4 H, Ar*H*), 3.96 (t, 2 H, ^3J = 5.6 Hz, CH_2N), 3.50 (t, 2 H, ^3J = 5.6 Hz, CH_2S). ^{13}C NMR ($CDCl_3$): δ 164.1 (CH=N), 132.2–127.4 (Ar*C*), 52.1 (CH_2N), 39.6 (CH_2S). IR (neat): 1638 cm^{-1} ($\nu_{C=N}$). Removal of solvent and attempted crystallization of the oily residue gave **3**.

3,4-Dihydro-2*H*-1,5-benzothiazocine (6). This compound was prepared from diimine **4** as described above for the synthesis of **5**. ^{1}H NMR ($CDCl_3$): δ 8.94 (s, 1 H, CH=N), 7.40–7.28 (m, 4 H, Ar*H*), 3.77 (t, 2 H, ^3J = 6.1 Hz, CH_2N), 2.93 (t, 2 H, ^3J = 6.1 Hz, CH_2S), 2.02 (q, 2 H, ^3J = 6.1 Hz, CH_2). IR (neat): 1635 cm^{-1} ($\nu_{C=N}$). Removal of solvent gave diimine **4**.

6,7,8,9,15,16,17,18-Octahydrodibenzo[*f*,*m*][14,8,11]dithiadiazacyclotetradecine (7). Diimine **3** (10 g, 0.031 mol) was added in small portions into a cooled (0 °C) suspension of $LiAlH_4$ (2.35 g, 0.062 mol) in tetrahydrofuran (750 mL). After the addition was complete, the mixture was heated under reflux for 2 h and then it was cooled (0 °C) and excess $LiAlH_4$ was destroyed by the sequential addition of water (2.3 mL), NaOH (15%, 2.3 mL), and water (7 mL). The precipitate was filtered off and washed with tetrahydrofuran (2 × 100 mL), and the filtrate was evaporated to dryness to afford a white solid. Recrystallization of the solid from dichloromethane–diethyl ether mixture gave colorless needles of the pure diamine: yield 9.3 g (92%); mp 135–136 °C. Anal. Calcd for $C_{18}H_{22}N_2S_2$: C, 65.4; H, 6.7; N, 8.5; S, 19.4. Found: C, 65.6; H, 6.9; N, 8.6; S, 19.3. ^{1}H NMR ($CDCl_3$): δ 7.26–6.99 (m, 8 H, Ar*H*), 3.85 (s, 4 H, $ArCH_2$), 3.24 (t, 4 H, ^3J = 5.3 Hz, CH_2N), 2.70 (t, 4 H, ^3J = 5.3 Hz, CH_2S). ^{13}C NMR ($CDCl_3$): δ 130.8–125.7 (Ar*C*), 52.1, 45.6 (CH_2N), 33.7 (CH_2S). IR (Nujol): 3300 cm^{-1} (ν_{NH}). Mass spectrum: *m/e* 330 [M]$^+$. Mol wt (osmometry, CH_2Cl_2): 330 (calcd); 328 (found).

7,8,9,10,16,17,18,19,20-Nonahydro-1*H*,6*H*-dibenzo[*g*,*o*][1,9,5,13]dithiadiazacyclohexadecine Hydrate (8). This compound was prepared from diimine **4** (10 g, 0.028 mol) by a method similar to one described for the homologue above: yield 9.4 g (93%); mp 69–70 °C. Anal. Calcd for $C_{20}H_{28}N_2OS_2$: C, 63.8; H, 7.5; N, 7.4; S, 17.0. Found: C, 63.8; H, 7.7; N, 7.4; S, 16.8. ^{1}H NMR ($CDCl_3$): δ 7.35–7.16 (m, 8 H, Ar*H*), 3.88 (s, 4 H), $ArCH_2$), 3.01 (t, 4 H, ^3J = 6.4 Hz, CH_2N), 2.78 (t, 4 H, ^3J = 6.4 Hz, CH_2S), 1.91 (q, 4 H, ^3J = 6.4 Hz, CH_2) (N*H* and O*H* resonances were obscured by the methylene signals). ^{13}C NMR ($CDCl_3$): δ 140.6–126.8 (Ar*C*), 52.6, 48.1 (CH_2N), 33.1 (CH_2S), 29.0 (CH_2). IR (Nujol): 3270, 3170 cm^{-1} (ν_{NH} and ν_{OH}). Mass spectrum: *m/e* 359 [M]$^+$. Mol wt (osmometry, CH_2Cl_2): 376 (calcd); 381 (found).

2,3,4,5-Tetrahydro-1,4-benzothiazepine (9). A solution of the diimine **3** (1 g, 3 mmol) in diethyl ether (50 mL) was heated under reflux with trifluoroacetic acid (0.1 mL) for 5 days. The reaction mixture was cooled to room temperature, and then it was slowly added to a stirred suspension of $LiAlH_4$ (350 mg, excess) in diethyl ether (100 mL). After the usual workup and distillation (Kugelrohr apparatus) the product was obtained as a viscous oil: yield 250 mg (25%); bp 170 °C (0.05 mmHg) (Kugelrohr). Anal. Calcd for $C_9H_{11}NS$: C, 65.4; H, 6.7. Found: C, 65.3; H, 6.9. ^{1}H NMR ($CDCl_3$): δ, 7.58–7.10 (m, 4 H, Ar*H*), 4.13 (s, 2 H, $ArCH_2$), 3.38 (t, 2 H, ^3J = 5.1 Hz, CH_2N), 2.76 (t, 2 H, ^3J = 5.1 Hz, CH_2S). IR (neat): 3320 cm^{-1} (ν_{NH}). Mass spectrum: *m/e* 165 [M]$^+$. For [1]·HCl: mp 239–240 °C (lit.[22] mp 237–238 °C).

3,4,5,6-Tetrahydro-2*H*-1,5-benzothiazocine (10). This compound was prepared in 20% yield from diimine **4** as described above. Anal. Calcd for $C_{10}H_{13}NS$: C, 67.0; H, 7.3; N, 7.8. Found: C, 66.7; H, 7.2; N, 7.7. ^{1}H NMR ($CDCl_3$): δ 7.38–7.05 (m, 4 H, Ar*H*), 3.82 (s, 2 H, $ArCH_2$), 2.96 (t, 2 H, ^3J = 6.3 Hz, CH_2N), 2.70 (t, 2 H, ^3J = 6.3 Hz, CH_2S), 1.80 (q, 2 H, ^3J = 6.3 Hz, CH_2), 1.60 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ 139.2–125.3 (Ar*C*), 51.9, 47.3 (CH_2N), 31.3 (CH_2S), 29.5 (CH_2). IR (neat): 3260 cm^{-1} (ν_{NH}).

Preparation of Copper(I) Complexes. Tetrakis(acetonitrile)copper(I) Trifluoromethanesulfonate Hemihydrate. This compound was prepared by a method similar to one described for the preparation of the corresponding hexafluorophosphate salt.[19] Triflic acid (CF_3SO_3H) (6.2 mL) was added dropwise to a suspension of Cu_2O (5 g, 0.04 mol) in acetonitrile (150 mL). After ca 1 h, the pale blue solution was filtered to remove traces of solid and then the filtrate was concentrated to ca 50 mL. The addition of diethyl ether to the concentrated solution caused the crystallization of the white crystalline product, which was filtered off, washed with diethyl ether, and dried, yielding 26 g (99%); mp 90–91 °C. Anal. Calcd for $C_9H_{13}CuF_3N_4O_{3.5}S$: C, 28.0; H, 3.4; N, 14.5. Found: C, 27.8; H, 3.2; N, 14.3.

(*T*-4)-[6,7,15,16-Tetrahydrodibenzo[*f*,*m*][1,8,4,11]dithiadiazacyclotetradecine-*S*^{5},*S*^{14},*N*^{8},*N*^{17}]copper(I) Trifluoromethanesulfonate (11). Diimine **3** (2 g, 6.1 mmol) and $[Cu(CH_3CN)_4]CF_3SO_3·0.5H_2O$ (2.3 g, 6.1 mmol) were dissolved in dichloromethane (25 mL). Filtration of the bright red solution, followed by dilution of the filtrate with diethyl ether, afforded the deep orange crystalline product, which was filtered off and washed with diethyl ether: yield 3.14 g (95%); mp 206–209 °C. Anal.

(22) Wuensch, K. H.; Ehlers, A.; Beyer, H. *Z. Chem.* **1967**, *7*, 185.

Calcd for $C_{19}H_{18}CuF_3N_2O_3S_3$: C, 42.3; H, 3.4; N, 5.2. Found: C, 42.3; H, 3.3; N, 5.4. ^{1}H NMR (CD_2Cl_2): δ 8.60 (br s, 2 H, CH=N), 7.94–7.57 (m, 8 H, Ar*H*), 3.80–3.35 (m, 8 H, CH_2N, CH_2S). ^{13}C NMR (CD_2Cl_2): δ 163.6 (CH=N), 138.9–127.8 (Ar*C*), 55.4 (CH_2N), 46.0 (CH_2S). IR (Nujol): 1650 cm^{-1} ($\nu_{C=N}$). Λ_M (MeOH): 62 cm^2 Ω^{-1} mol^{-1}.

(*T*-4)-[7,8,16,17,18-Pentahydro-1*H*,6*H*-dibenzo[*g*,*o*][1,9,5,13]dithiadiazacyclohexadecine-*S*^{5},*S*^{15},*N*^{9},*N*^{19}]copper(I) Trifluoromethanesulfonate (12). Diimine **4** (2 g, 5.6 mmol) and the copper(I) triflate (2.1 g, 5.6 mmol) were reacted together in dichloromethane. The product crystallized from a 2-propanol–diethyl ether mixture as orange needles, which were recrystallized from hot water: yield 3.1 g (97%); mp 178–179 °C. Anal. Calcd for $C_{21}H_{22}CuF_3N_2O_3S_3$: C, 44.5; H, 3.9; N, 4.9. Found: C, 44.4; H, 3.9; N, 5.1. ^{1}H NMR (CD_2Cl_2): δ 8.43 (s, 2 H, CH=N), 7.80–7.45 (m, 8 H, Ar*H*), 4.04 (m, 4 H, CH_2N), 3.19 (m, 4 H, CH_2S), 2.07 (m, 4 H, CH_2). ^{13}C NMR (CD_2Cl_2): δ 165.7 (CH=N), 139.1–129.1 (Ar*C*), 65.5 (CH_2N), 42.7 (CH_2S), 28.8 (CH_2). IR (Nujol): 1630 cm^{-1} ($\nu_{C=N}$). Λ_M (MeOH): 62 cm^2 Ω^{-1} mol^{-1}.

[6,7,15,16-Tetrahydrodibenzo[*f*,*m*][1,8,4,11]dithiadiazacyclotetradecine-*S*^{5},*S*^{14},*N*^{8},*N*^{17}](triphenylphosphine)copper(I) Trifluoromethanesulfonate (13). Triphenylphosphine (0.97 g, 3.7 mmol) was added to a solution of **11** (2 g, 3.7 mmol) in dichloromethane (15 mL). Dilution of the yellow-orange solution with diethyl ether caused precipitation of yellow needles of the product. The crystals were filtered off, washed with diethyl ether, and dried in vacuo: yield 2.82 g (95%); mp 170 °C. Anal. Calcd for $C_{37}H_{33}CuF_3N_2O_3PS_3$: C, 55.5; H, 4.2; N, 3.5. Found: C, 55.3; H, 4.0; N, 3.6. ^{1}H NMR (CD_2Cl_2): δ 8.63 (s, 2 H, CH=N), 7.75–6.80 (m, 23 H, Ar*H*), 3.75 (m, 4 H, CH_2N), 3.30 (m, 4 H, CH_2S). ^{13}C NMR (CD_2Cl_2): δ 167.1 (CH=N), 138.0–128.0 (Ar*C*), 58.0 (CH_2N), 40.9 (CH_2S). ^{31}P NMR (CD_2Cl_2): δ 1.1 (br s, PPh_3). IR (Nujol): 1640 cm^{-1} ($\nu_{C=N}$). Λ_M (MeOH): 63 cm^2 Ω^{-1} mol^{-1}.

[7,8,16,17,18-Pentahydro-1*H*,6*H*-dibenzo[*g*,*o*][1,9,5,13]dithiadiazacyclohexadecine-*S*^{5},*S*^{15},*N*^{9},*N*^{19}](triphenylphosphine)copper(I) Trifluoromethanesulfonate (14). This compound was prepared from (**12**) (2 g, 3.5 mmol) and PPh_3 as described above; it crystallized as orange needles: yield 2.73 g (93%); mp 150–155 °C. Anal. Calcd for $C_{39}H_{37}CuF_3N_2O_3PS_3$: C, 56.5; H, 4.5; N, 3.4. Found: C, 56.2; H, 4.4; N, 3.6. ^{1}H NMR (CD_2Cl_2): δ 8.41 (s, 2 H, CH=N), 7.55–6.88 (m, 23 H, Ar*H*), 3.88 (m, 4 H, CH_2N), 3.20 (m, 4 H, CH_2S), 2.20 (m, 4 H, CH_2). ^{13}C NMR (CD_2Cl_2): δ 165.0 (CH=N), 139.0–129.0 (Ar*C*), 63.7 (CH_2N), 38.8 (CH_2S), 28.9 (CH_2). ^{31}P NMR (CD_2Cl_2): δ 2.11 (br s, PPh_3). IR (Nujol): 1630 cm^{-1} ($\nu_{C=N}$). Λ_M (MeOH): 64 cm^2 Ω^{-1} mol^{-1}.

Structural Analysis. A cross section was cleaved from a needle of **11** and mounted on the end of a quartz fiber. X-ray photographs revealed only $\bar{1}$ Laue symmetry, indicating that the space group was either *P*1 or *P*$\bar{1}$. Successful solution and refinement of the structure established it to be *P*$\bar{1}$. A fragment was also cut from a thin plate of **12** and mounted on a fiber. X-ray photographs showed Laue 2/*m* symmetry, and systematic absences uniquely determined the space group to be $P2_1/c$. Crystal data are given in Table I. The intensities of reflections $+h,\pm k,\pm l$ were collected for **11** and $\pm h,+k,+l$ for **12**. Three standards measured after every 97 reflections showed a small decrease in intensity (ca. 2%) during data acquisition on **11**; data were rescaled accordingly.[23] Rescaling was not required for **12**. Absorption corrections[24] were applied to each data set (range in *T*: 0.442–0.571 for **11**; 0.499–0.779 for **12**). The structures were solved by heavy-atom methods. The non-H atoms were located in electron-density maps and then were refined by block-diagonal least squares, initially with isotropic and later with anisotropic temperature factors. In **12**, C(11) was found to be disordered over two sites of occupancies 0.65 and 0.35. Hydrogen atoms were added at geometrically calculated positions (r_{C-H} = 0.95 Å) with isotropic temperature factors set at 1.2 times the B_{eq} values of the atoms to which they were respectively bonded. Hydrogen atom parameters were not refined but were redetermined periodically during refinement. Examination of the structure factor listings indicated that the data for both compounds suffered extinction effects; a Zachariasen extinction parameter,[25] β, was accordingly introduced. Refinement of each structure was continued by using full-matrix least squares until all shift/error ratios were <0.03. The final values for β were 2.14 (8) $\times$ 10^{-5} for **11** and 3.2 (2) $\times$ 10^{-5} for **12**. Least-squares refinement was performed by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where w = 1 in the early stages and $w = 1/[(\sigma(F_o))^2 + 0.25(pF_o)^2]$ in the final cycles. The parameter p was varied to give a minimum variation in average $w(|F_o| - |F_c|)^2$ as a function of F_o and $(\sin\theta)/\lambda$ (final p = 0.03 for **11** and 0.035 for **12**). The biggest features in a final difference map of **11** were in the vicinity of the fluorine atoms of the anion. Introduction of disorder to the CF_3 group did not improve the model significantly. Peaks in a final difference map of **12** were situated near atoms of the anion. Neutral-atom scattering factors with anomalous dispersion corrections were used throughout.[26] Final atomic coordinates for the two complexes are listed in Tables II and III. ORTEP diagrams[27] of the two cations are given in Figures 1 and 2.

Computer Programs. The ANUCRYS structure determination package[28] was used for all aspects of the crystal structure analyses.

Registry No. **1**, 96751-78-9; **2**, 109467-80-3; **3**, 96740-34-0; **4**, 109467-81-4; **5**, 97184-58-2; **6**, 109467-82-5; **7**, 96740-36-2; **8**, 109467-83-6; **9**, 58980-39-5; **10**, 109467-84-7; **11**, 109467-86-9; **12**, 109467-88-1; **13**, 109467-90-5; **14**, 109467-92-7; $BaMnO_4$, 7787-35-1; 2-mercaptobenzenemethanol, 4521-31-7; 2-chloroethanamine hydrochloride, 870-24-6; 3-chloropropanamine hydrochloride, 6276-54-6; tetrakis(acetonitrile)copper(I) trifluoromethanesulfonate, 58452-28-1.

Supplementary Material Available: For $[Cu(C_{18}H_{18}N_2S_2)](CF_3SO_3)$ (**11**) and $[Cu(C_{20}H_{22}N_2S_2)](CF_3SO_3)$ (**12**), tables of bond distances and angles, thermal parameters of the non-hydrogen atoms, calculated hydrogen atom parameters, least-squares planes, and selected torsion angles (12 pages); tables of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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