< $7b_1$ for the O_2 and complexes, but it is $7b_1 < 11a_1$ for the S_2 and Se_2 complexes. Orbital $11a_1$ is primarily M–P_{ax} antibonding in character while $7b_1$ is strongly X–X and M–X_2 antibonding. The ordering of the levels in the two cases is different because of the different P_{ax}–Ir–P_{ax} angles used in the calculations. For both the Rh and Ir dioxygen complexes the P_{ax}–Ir–P_{ax} angle was taken to be 161°, the same as the angle in $[M(O_2)(P(CH_3)_2C_6H_5)_4]^+$ (M = Rh, Ir), but for the S_2 and Se_2 complexes the angle used was 172°, the same as the angle in $[Ir(X_2)(dppe)]^+$ (X = S, Se) and close to the angle (175°) in $[Ir(O_2)(dppe)_2]^+$. The more nearly linear angle in the S_2 and Se_2 complexes increases the M–P_{ax} antibonding interaction in orbital $11a_1$ and raises it above $7b_1$. Since the behavior of $[Ir(O)_2(dppe)_2]^+$ on electrochemical reduction indicates that it has a strongly Ir–O_2 antibonding LUMO,[42] it is likely that the LUMO of this complex is orbital $7b_1$, as would be anticipated from its nearly linear P_{ax}–M–P_{ax} angle.

Acknowledgment. We are indebted to Professor J. G. Norman, Jr., for informing us of the details of his calculations on dioxygen complexes prior to publication.

Registry No. $[Rh(S_2)(PH_3)_4]^+$, 83632-71-7; $[Rh(Se_2)(PH_3)_4]^+$, 83632-72-8; $[Ir(S_2)(PH_3)_4]^+$, 83632-73-9; $[Ir(S_2)(PH_3)_4]^+$, 83632-74-0; $[Ir(PH_3)_4]^{3+}$, 82269-54-3; S_2^{2-}, 16734-12-6.

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1,4,7-Trithiacyclononane, a Novel Tridentate Thioether Ligand, and the Structures of Its Nickel(II), Cobalt(II), and Copper(II) Complexes

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An improved method for preparing 1,4,7-trithiacyclononane (1,4,7-TTCN) is reported. The yields of certain medium-sized-ring dithioethers are also improved by this method. The bis(1,4,7-trithiacyclononane)nickel(II), -cobalt(II), and -copper(II) complexes have been prepared and their structures determined by X-ray crystallographic analyses. The $[Ni(1,4,7\text{-TTCN})_2](BF_4)_2$ complex crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.681$ (2) Å, $b = 11.685$ (3) Å, $c = 11.624$ (3) Å, $\beta = 106.57$ (2)°, and $Z = 2$. The $[Co(1,4,7\text{-TTCN})_2](BF_4)_2$ complex crystallizes in the orthorhombic space group *Pbca* with $a = 19.789$ (40) Å, $b = 15.235$ (12) Å, $c = 9.202$ (3) Å, and $Z = 4$. The $[Cu(1,4,7\text{-TTCN})_2](BF_4)_2$ complex crystallizes in the orthorhombic space group *Pbca* with $a = 21.169$ (3) Å, $b = 15.193$ (2) Å, $c = 8.729$ (2) Å, and $Z = 4$. Full-matrix least-squares refinement led to convergence with $R = 0.030$, 0.094, and 0.062, respectively, after several cycles of anisotropic refinement. In each complex the metal atom occupies a slightly distorted octahedral environment of sulfur atoms provided by two facially coordinating 1,4,7-TTCN ligands. The geometrical constraints of the ligand induce nearly regular octahedral coordination even with copper(II).

Introduction

Transition-metal complexes with thioether ligands are of much current interest. Such complexes have been extensively reviewed recently.[1] Of particular interest from a biological perspective are the copper complexes of thioethers. Macrocyclic tetrathioether complexes of Cu(II), even those with undistorted tetragonal coordination geometry about the copper atom,[2] show the same unusual spectroscopic[3] and electrochemical properties[4] as the "blue" copper proteins. Coordination of all four sulfur atoms of a macrocyclic tetrathioether such as 1,4,8,11-tetrathiacyclotetradecane (14-ane-S_4) by a single metal atom requires a change in conformation of the ligand. Crystal structure studies show that the conformation of the uncomplexed 14-ane-S_4[5] is one in which the sulfur atoms are all directed away from the center of the ring, i.e., exodentate. However, in its Cu(II)[2] and Ni(II)[6] complexes, in which all four sulfur atoms are coordinated to the metal atom in a planar array, the ligand adopts an endodentate conformation. Our structural studies of crystalline[7] and gaseous[8] 1,4,7-trithiacyclononane (1,4,7-TTCN) revealed that, unlike macrocyclic polythioethers,[5,9] it adopts a conformation with the sulfur atoms endodentate. In this conformation 1,4,7-TTCN can be a tridentate ligand without conformational change[10] and owing to the geometric placement of the three ligating sulfur atoms suitable metal complexes may be unusually stable.[11]

This paper reports an improved procedure for preparing 1,4,7-TTCN and the crystal and molecular structure of $[Ni(1,4,7\text{-TTCN})_2](BF_4)_2$, $[Co(1,4,7\text{-TTCN})_2](BF_4)_2$, and $[Cu(1,4,7\text{-TTCN})_2](BF_4)_2$.

Experimental Section

Preparation of 1,4,7-Trithiacyclononane—Typical Procedure for Preparation of Mesocyclic Polythioethers. A 2-L three-necked round-bottom flask, equipped with matching calibrated 125-mL

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constant-addition funnels, reflux condensers, magnetic stir bar, and a nitrogen inlet–outlet, was charged with absolute methanol (300 mL). Into one funnel were added 2.20 M benzyltrimethylammonium methoxide methanolic solution (50 mL, 0.110 mol; Aldrich Chemical Co.), bis(2-mercaptoethyl) sulfide (6.25 mL, 7.62 g, 0.050 mol; Parish Chemical Co.), and sufficient absolute methanol to dilute to 125 mL. Into the other funnel were added 1,2-dichloroethane (3.95 mL, 4.95 g, 0.050 mol; Matheson Coleman and Bell Chemical Co.) and sufficient absolute methanol to dilute to 125 mL. The two solutions were added simultaneously to the rapidly stirring, refluxing methanol at a rate of about 10 drops/min. Upon completion of the addition, the funnels were refilled as above and addition was continued (the funnels were refilled four times for a total of five separate additions). The methanol was removed from the reaction mixture by rotary evaporation. The residual solid was triturated with diethyl ether and filtered. The ether was evaporated from the filtrate and the residue chromatographed on a silica gel column (5-cm diameter × 50-cm length, 500 g), eluting with 5% ethyl acetate in hexane. Collection and rotary evaporation of the first 2.5 L of eluent yielded 1.98 g of 1,4,7-trithiacyclononane (0.011 mol; 4.4% yield) as a colorless crystalline solid. A sample of the product was sublimed (70 °C (1 atm)) to obtain analytically pure 1,4,7-trithiacyclononane: mp 84 °C; IR (KBr) 2900, 1450, 1400, 1275, 925, 880, 823 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.15 (s, CH_2); mass spectrum m/e 180 (M^+). Anal. Calcd for $C_6H_{12}S_3$: C, 39.96; H, 6.71; S, 53.33. Found: C, 39.92; H, 6.71; S, 53.32.

Preparation of $Ni(1,4,7\text{-}TTCN)_2(BF)_2$. A solution of nickel(II) tetrafluoroborate hexahydrate (137 mg, 0.588 mmol; Alfa Chemical Co.) in 10 mL of absolute ethanol was added to a solution of 1,4,7-trithiacyclononane (212 mg, 1.176 mmol) in 15 mL of absolute ethanol. The reaction mixture turned pale violet initially. The solution was heated to gentle reflux, upon which the color immediately changed to pink. Red crystals were grown from the reaction mixture by solvent diffusion with diethyl ether to give 348 mg (100% yield) of bis(1,4,7-trithiacyclononane)nickel(II) tetrafluoroborate as a brick red crystalline solid: IR (KBr) 3000, 2950, 1450, 1420, 1290, 1160–1000 (s, BF_4^-), 940, 900, 830 cm^{-1}; UV/vis λ_{max} (ϵ) (CH_3NO_2) 530 nm (28), 374 (61). Anal. Calcd for $C_{12}H_{24}S_6NiB_2F_8$: C, 24.30; H, 4.08; S, 32.44. Found: C, 24.34; H, 4.10; S, 32.35.

Preparation of $Co(1,4,7\text{-}TTCN)_2(BF)_2$. A solution of cobalt(II) tetrafluoroborate hexahydrate (32.7 mg, 0.081 mmol; Alfa Chemical Co.) in 5 mL of absolute ethanol was added to a solution of 1,4,7-trithiacyclononane (34.6 mg, 0.192 mmol) in 5 mL of absolute ethanol, resulting in the immediate precipitation of a violet solid. The precipitate was filtered off, washed with absolute ethanol, and recrystallized from nitromethane/diethyl ether to give 27.5 mg (57% yield) of bis(1,4,7-trithiacyclononane)cobalt(II) tetrafluoroborate as a purple crystalline solid: IR (KBr) 2960, 1440, 1405, 1300, 1130–1030 (s, BF_4^-), 940, 910, 830, 520 cm^{-1}; UV/vis λ_{max} (ϵ) (CH_3NO_2) 478 nm (93), 372 (2610), 356 (634). Anal. Calcd for $C_{12}H_{24}S_6CoB_2F_8$: C, 24.29; H, 4.08; S, 32.43. Found: C, 24.41; H, 4.11; S, 32.33.

Preparation of $Cu(1,4,7\text{-}TTCN)_2(BF_4)_2$. A solution of copper(II) tetrafluoroborate hydrate (47.8 mg, 0.139 mmol; Alfa Chemical Co.) in 4 mL of absolute ethanol was added to a solution of 1,4,7-trithiacyclononane (50.0 mg, 0.278 mmol) in 6 mL of absolute ethanol, forming a brown solution, immediately followed by precipitation of a metallic brown solid. The precipitate was filtered, washed with absolute ethanol, and recrystallized from acetonitrile/diethyl ether to give 64.8 mg (80% yield) of bis(1,4,7-trithiacyclononane)copper(II) tetrafluoroborate as a dark brown crystalline solid: IR (KBr) 2970, 1550, 1400, 1300, 1150–1030 (s, BF_4^-), 940, 900, 830 cm^{-1}; UV/vis λ_{max} (ϵ) (CH_3NO_2) 446 nm (4692). Anal. Calcd for $C_{12}H_{24}S_6CuB_2F_8$: C, 24.11; H, 4.05; S, 32.18. Found: C, 24.09; H, 4.05; S, 32.11.

Collection and Reduction of X-ray Data. Clear red crystals of $Ni(1,4,7\text{-}TTCN)_2(BF_4)_2$ were obtained by vapor diffusion of a solution of the compound in absolute ethanol with diethyl ether. Similarly, violet crystals of $Co(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3NO_2$ and dark brown crystals of $Cu(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3CN$ were obtained by the vapor diffusion technique of diethyl ether into solutions of the compounds in nitromethane and acetonitrile, respectively. In each study a well-formed crystal was mounted on a Syntex $P2_1$ autodiffractometer. It was necessary to seal both the cobalt and copper complexes in capillaries to prevent decomposition of the lattice by loss of solvent. The automatic centering and least-squares routines were carried out on 25 reflections for $Ni(1,4,7\text{-}TTCN)_2(BF_4)_2$ and 15 reflections for both $Co(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3NO_2$ and $Cu(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3CN$ to obtain the cell dimensions that are given in Table II. The data were reduced to F_o^2 and $\sigma(F_o^2)$. Lorentz and polarization corrections were applied to all reflections. The θ–2θ data collection technique was used to collect the data of which those with $I \geq 3\sigma(I)$ were used in the calculations.

Table I. Preparation of Cyclic Dithioethers from the Benzyltrimethylammonium Salts of Dithiols and Dibromides[a]

dithiol $HS(CH_2)_mSH$ m	dibromide $Br(CH_2)_nBr$ n	product	yield,[b] %
2	3	1,4-dithiacycloheptane	65 (9,[c] 16[d])
3	3	1,5-dithiacyclooctane	46[e,f] (6.8,[g] 27[h])
2	4	1,4-dithiacyclooctane	7 (8.5[i])
4	2		14
3	4	1,5-dithiacyclononane	0.5 (5.8[i])
4	3		9
4	4	1,6-dithiacyclodecane	1.5 (1.9[j])

[a] The dithiol was treated with 2 equiv of base, and the dithiolate so obtained was allowed to react with the dibromide. A typical procedure is given in the Experimental Section for the preparation of 1,4,7-TTCN. [b] These are isolated yields of pure material. [c] Meadow, J. R.; Reid, E. E. *J. Am. Chem. Soc.* 1934, *56*, 2177. [d] Ochrymowycz, L. A.; Mak, C.-P.; Michna, J. D. *J. Org. Chem.* 1974, *39*, 2079. [e] The yield by GC analysis of the distilled reaction product is 57%. [f] Use of the tetramethylammonium salt of the dithiol gives 1,5-DTCO in 25% yield; use of the tetra-*n*-butylammonium salt of the dithiol gives 1,5-DTCO in 37% yield. [g] Tucker, N. B.; Reid, E. E. *J. Am. Chem. Soc.* 1933, *55*, 775. [h] Reference 27. [i] Musker, W. K.; Roush, P. B. *J. Am. Chem. Soc.* 1976, *98*, 6745. [j] Bradshaw, J. S.; Hui, J. Y. *J. Heterocycl. Chem.* 1974, *11*, 649.

Solution and Refinement of the Structure. In each case, the structure was solved by the heavy-atom method. The metal atom in each structure was constrained by the symmetry requirements of the respective space groups to occupy a special position (inversion center). The three unique sulfur atoms were located from three-dimensional Patterson maps. The remaining atoms were located by subsequent structure factor calculations and difference electron density maps. The structures were refined by full-matrix least-squares techniques[12] using neutral-atom scattering factors for all species,[13] leading to isotropic convergence at $R = 0.096$ for $Ni(1,4,7\text{-}TTCN)_2(BF_4)_2$, $R = 0.131$ for $Co(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3NO_2$, and $R = 0.167$ for $Cu(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3CN$.[14] Several cycles of anisotropic refinement led to convergence at $R = 0.045$, 0.099, and 0.075, respectively. In each study the hydrogen atoms were added to the model in geometrically ideal positions. The hydrogen atom thermal parameters were set according to $B_H = B_N + 1$, where N is the atom to which H is bonded. The hydrogen atom parameters were not refined. Several cycles of anisotropic refinement led to convergence with $R = 0.030$, $R_w = 0.037$, and GOF = 1.63 for $Ni(1,4,7\text{-}TTCN)_2(BF_4)_2$, $R = 0.094$, $R_w = 0.103$, and GOF = 3.14 for $Co(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3NO_2$, and $R = 0.062$, $R_w = 0.066$, and GOF = 2.08 for $Cu(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3CN$.

Results and Discussion

Synthesis of 1,4,7-TTCN. Reaction of disodium 3-thiapentane-1,5-dithiolate with 1,2-dichloroethane produces 1,4,7-TTCN in 0.04% yield.[15] Use of the bis(benzyltrimethylammonium) salt of 3-thiapentane-1,5-dithiol instead

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(12) The major programs used during the solution and refinement of the structure were FORDAP (Fourier summation program by A. Zalkin) and NUCLS (structure factor calculations and full-matrix least-squares refinement by J. A. Ibers, itself a modification of ORFLS, by W. R. Busing, K. O. Martin, and H. A. Levy).

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(14) The cobalt and copper complexes crystallize with solvent. So that decomposition of the lattice by loss of solvent could be prevented, they were sealed in capillaries. The higher R factors for these complexes compared to the nickel complex are due to absorption by the capillary tubes and thermal motion of the solvent molecules.

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Table II. Crystal Data for the 1,4,7-TTCN Metal Complexes[a]

	$Ni(1,4,7\text{-}TTCN)_2(BF_4)_2$	$Co(1,4,7\text{-}TTCN)_2(BF_4)_2 \cdot 2CH_3NO_2$	$Cu(1,4,7\text{-}TTCN)_2(BF_4)_2 \cdot 2CH_3CN$
formula	$C_{12}H_{24}S_6NiB_2F_8$	$C_{14}H_{30}N_2O_4S_6CoB_2F_8$	$C_{16}H_{30}N_2S_6CuB_2F_8$
fw	593.00	715.31	679.94
space group	$P2_1/c$ (No. 14)[b]	*Pbca* (no. 61)[c]	*Pbca* (No. 61)[c]
cell dimens			
a, Å	8.681 (2)	19.789 (40)	21.169 (3)
b, Å	11.685 (3)	15.235 (12)	15.193 (2)
c, Å	11.624 (3)	9.202 (3)	8.729 (2)
β, deg	106.57 (2)		
V, Å^3	1130.1 (5)	2274 (6)	2807.6 (8)
Z	2	4	4
d_{obsd}, g cm^{-3}	1.74 (1)[d]	*e*	*e*
d_{calcd}, g cm^{-3}	1.743	2.089	1.608
cryst color, shape	red, prism	violet, rectangular parallelepiped	brown, rectangular parallelepiped
cryst dimens, mm	0.3 × 0.2 × 0.1	0.3 × 0.3 × 0.1	0.3 × 0.2 × 0.2
radiatn, Å	λ (Mo Kα) 0.710 69	λ (Mo Kα) 0.710 69	λ (Mo Kα) 0.710 69
monochromator	graphite cryst	graphite cryst	graphite cryst
supplied power	50 kV, 30 mA	50 kV, 30 mA	50 kV, 30 mA
data collecn method	θ–2θ scan	θ–2θ scan	θ–2θ scan
scan speed, deg min^{-1}	variable (2.0–29.3), determined as a function of peak intens	variable (3.9–29.3), determined as a function of peak intens	variable (5.9–29.3), determined as a function of peak intens
scan range (2θ), deg	Mo Kα – 1.0 to Mo Kα + 1.0	Mo Kα – 1.0 to Mo Kα + 1.0	Mo Kα – 1.0 to Mo Kα + 1.0
ratio of total bkgd time to peak scan time	0.5	0.5	0.5
std reflcns	(300), (040), (004); after every 97 readings	(–3,–1,–1), (022), (111); after every 97 readings	(600), (060), (004); after every 97 readings
max dev of stds, %	3.3 (random)	2.9 (random)	2.4 (random)
2θ limit, deg	4.0–50.0	4.0–50.0	4.0–50.0
no. of unique data	2090	2462	2500
no. of data used in the calculations	1638	1027	1210
abs coeff (μ_λ), cm^{-1}	14.5	14.2	13.0

[a] The standard deviation of the least significant figure is given in parentheses. [b] The space group was unambiguously determined from systematic absences: *h*0*l*, $l \neq 2n$; 0*k*0, $k \neq 2n$. [c] The space group was unambiguously determined from systematic absences: 0*kl*, $k \neq 2n$; *h*0*l*, $l \neq 2n$; *hk*0, $h \neq 2n$. [d] The density was determined by the flotation method using a solution of carbon tetrachloride and bromoform. [e] The density was not experimentally determined due to instability of the crystal.

of the disodium salt, under high-dilution conditions, results in a 100-fold increase in the yield of 1,4,7-TTCN.[16] So it could be determined whether the use of quaternary ammonium salts in place of alkali metal salts would similarly be effective in improving the yield of mesocyclic[17] dithioethers, the studies in Table I have been done. In some, but not all, cases the yield is significantly improved. The yield of 1,4-dithia-7-oxacyclononane from 1,2-ethanedithiol and 1,5-dichloro-3-oxabutane is also not improved by use of the benzyltrimethylammonium salt rather than the sodium salt[18] of the dithiol. In the cases studied, benzyltrimethylammonium salts are superior to tetra-*n*-butylammonium salts which, in turn, are better than tetramethylammonium salts. For dithioethers such as 1,5-DTCN, which can be synthesized by either of two combinations of dithiol and dibromide, in the case of 1,5-DTCN either 1,3-propanedithiol and 1,4-dibromobutane or 1,4-butanedithiol and 1,3-dibromopropane, significant differences in yield are obtained by use of one combination or the other. Although there is a dramatic improvement in the yield of certain mesocyclic polythioethers by the use of quaternary ammonium salts rather than sodium or potassium salts, this method is not a panacea for the synthesis of all medium-size-ring polythioethers.[19]

Table III. Fractional Atomic Coordinates for $Ni(1,4,7\text{-}TTCN)_2(BF_4)_2$

atom	*x*	*y*	*z*
Ni	0.0[a]	0.0	0.0
S(1)	0.2717 (1)[b]	–0.0400 (1)	0.0090 (1)
S(2)	0.0937 (1)	0.1164 (1)	0.1740 (1)
S(3)	0.0633 (1)	–0.1599 (1)	0.1308 (1)
C(1)	0.3694 (4)	0.0788 (3)	0.1033 (4)
C(2)	0.3114 (4)	0.1031 (3)	0.2128 (3)
C(3)	0.0426 (5)	0.0259 (3)	0.2839 (3)
C(4)	0.0896 (4)	–0.0996 (3)	0.2804 (3)
C(5)	0.1752 (4)	–0.2371 (3)	0.1066 (3)
C(6)	0.3213 (4)	–0.1646 (3)	0.1071 (4)
B	0.3194 (5)	0.4138 (4)	0.1187 (5)
F(1)	0.1869 (3)	0.3535 (2)	0.0577 (2)
F(2)	0.4572 (3)	0.3600 (2)	0.1133 (2)
F(3)	0.3206 (3)	0.4146 (4)	0.2374 (3)
F(4)	0.3125 (4)	0.5196 (2)	0.0746 (5)
H(1)	0.3516[c]	0.1516	0.0522
H(2)	0.4893	0.0648	0.1308
H(3)	0.3618	0.1767	0.2538
H(4)	0.3473	0.0390	0.2728
H(5)	–0.0779	0.0286	0.2699
H(6)	0.0954	0.0570	0.3663
H(7)	0.0509	–0.1443	0.3402
H(8)	0.2110	–0.1042	0.3035
H(9)	0.1380	–0.2764	0.0263
H(10)	0.2092	–0.2973	0.1707
H(11)	0.4000	–0.2142	0.0814
H(12)	0.3721	–0.1386	0.1920

[a] The nickel atom occupies the special position $x = 0.0$, $y = 0.0$, and $z = 0.0$ and was not varied. [b] Estimated standard deviations are in parentheses. [c] Hydrogen atom parameters were not refined.

Complexes of 1,4,7-TTCN. The metal complexes of 1,4,7-TTCN are conveniently prepared in good yields by reaction of 1,4,7-TTCN and the divalent metal salts in a 2:1

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(16) The yield of this reaction, after isolation and purification, is 4.4%. If 1,2-dibromoethane is substituted for 1,2-dichloroethane, then the yield, after isolation and purification, is 0.75%. According to footnote *d* of Table I, no 1,4,7-TTCN is formed on reaction of 1,2-dibromoethane with the disodium salt of 1,2-ethanedithiol.

(17) "Mesocycle" has been defined as medium-sized ring: Leonard, N. J.; Milligan, T. W.; Brown, T. L. *J. Am. Chem. Soc.* **1960**, *82*, 4075.

(18) Bradshaw, J. S.; Hui, J. Y.; Haymore, B. L.; Christensen, J. J.; Izatt, R. M. *J. Heterocycl. Chem.* **1973**, *10*, 1.

(19) Recently, 1,5-DTCN has been prepared in 45% yield from propane-1,3-dithiol, 1,4-dibromobutane, and cesium carbonate in *N,N*-dimethylformamide: Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1981**, *46*, 4481.

Table IV. Fractional Atomic Coordinates for $Co(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3NO_2$

atom	x	y	z
Co	0.0^a	0.0	0.0
S(1)	0.0047 (3)^b	−0.0323 (3)	0.2502 (6)
S(2)	0.1053 (3)	0.0508 (3)	0.0292 (6)
S(3)	−0.0442 (3)	0.1425 (3)	0.0383 (6)
C(1)	0.0617 (11)	0.0388 (13)	0.3153 (26)
C(2)	0.1241 (11)	0.0377 (14)	0.2197 (25)
C(3)	0.1573 (9)	−0.0319 (12)	−0.0582 (22)
C(4)	0.1344 (9)	−0.1274 (12)	−0.0147 (25)
C(5)	−0.0197 (9)	0.1953 (11)	−0.1289 (21)
C(6)	−0.0335 (13)	0.1399 (13)	−0.2677 (23)
B	0.3218 (21)	0.1144 (19)	0.0567 (36)
F(1)	0.3112 (12)	0.0327 (13)	0.0746 (23)
F(2)	0.3142 (9)	0.1390 (13)	−0.0802 (16)
F(3)	0.2775 (15)	0.1536 (18)	0.1371 (25)
F(4)	0.3808 (13)	0.1326 (17)	0.1023 (24)
C(7)	0.2016 (13)	0.3251 (15)	0.2105 (28)
N	0.1586 (18)	0.3049 (16)	0.1001 (38)
O(1)	0.1769 (21)	0.1795 (17)	0.4752 (27)
O(2)	0.1056 (12)	0.2743 (21)	0.1144 (40)
H(1)	0.0766^c	0.0177	0.4235
H(2)	0.0429	0.1058	0.3191
H(3)	0.1569	0.0925	0.2548
H(4)	0.1507	−0.0236	0.2370
H(5)	0.2093	−0.0222	−0.0256
H(6)	0.1524	−0.0241	−0.1754
H(7)	0.1610	−0.1739	−0.0831
H(8)	0.1471	−0.1383	0.0987
H(9)	0.0337	0.2089	−0.1203
H(10)	−0.0484	0.2559	−0.1347
H(11)	−0.0877	0.1326	−0.2835
H(12)	−0.0115	0.1738	−0.3603
H(13)	0.2400	0.2800	0.2800
H(14)	0.1705	0.3543	0.3014
H(15)	0.2357	0.3785	0.1741

[a] The cobalt atom occupies the special position $x = 0.0, y = 0.0$, and $z = 0.0$ and was not varied. [b] Estimated standard deviations are in parentheses. [c] Hydrogen atom parameters were not refined.

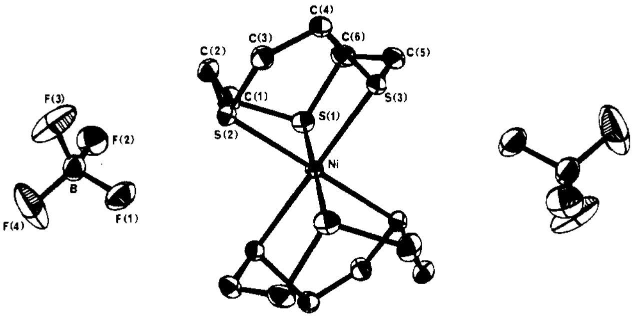

Figure 1. ORTEP[19] perspective drawing of $Ni(1,4,7\text{-}TTCN)_2(BF_4)_2$. The hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn to enclose 30% of the probability distribution.

ratio. The complexes thus formed are stable to coordinating solvents such as water and acetonitrile, in marked contrast to the reported[20] instability of Ni(II) complexes of macrocyclic polythioethers to hydroxylic solvents. This difference in stability is a manifestation of the unique conformation of 1,4,7-TTCN.[7,8]

The crystal and molecular structures of $[Ni(1,4,7\text{-}TTCN)_2](BF_4)_2$, $[Co(1,4,7\text{-}TTCN)_2](BF_4)_2\cdot 2CH_3NO_2$, and $[Cu(1,4,7\text{-}TTCN)_2](BF_4)_2\cdot 2CH_3CN$ were determined by X-ray crystallographic analysis. The crystal data for these compounds are given in Table II. The final atomic parameters are given in Tables III–V. The essential geometrical parameters for each complex are listed in Tables VI–VIII, respectively. Perspective drawings[21] of the complexes are shown in Figures 1–3, respectively, along with the labeling schemes. In each complex, the metal atom occupies a crystallographic inversion center. This study shows that the metal atom, in each case, lies in a slightly distorted octahedral environment of sulfur atoms provided by two facially coordinating tridentate 1,4,7-TTCN ligands. The S–M–S angles for sulfur atoms of the same ligand molecule average 88.5° while the S–M–S

Table V. Fractional Atomic Coordinates for $Cu(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3CN$

atom	x	y	z
Cu	0.0^a	0.0	0.0
S(1)	0.0053 (1)^b	−0.0272 (2)	0.2727 (3)
S(2)	0.1035 (1)	0.0679 (2)	0.0179 (3)
S(3)	−0.0550 (1)	0.1408 (2)	0.0387 (3)
C(1)	0.0644 (5)	0.0549 (6)	0.3225 (11)
C(2)	0.1222 (5)	0.0566 (6)	0.2191 (11)
C(3)	0.1500 (5)	−0.0184 (8)	−0.0726 (12)
C(4)	0.1377 (5)	−0.1099 (7)	−0.0205 (13)
C(5)	−0.0368 (5)	0.1893 (6)	−0.1470 (11)
C(6)	−0.0479 (5)	0.1315 (6)	−0.2849 (11)
B	0.3130 (9)	0.1294 (26)	0.0505 (19)
F(1)	0.3189 (8)	0.0380 (9)	0.0200 (18)
F(2)	0.3016 (5)	0.1469 (11)	−0.0853 (12)
F(3)	0.2667 (4)	0.1177 (8)	0.1489 (11)
F(4)	0.3664 (6)	0.1319 (12)	0.1027 (11)
C(7)	−0.2037 (8)	−0.1719 (10)	0.3816 (23)
C(8)	−0.1409 (7)	−0.1950 (10)	0.3730 (18)
N	−0.0907 (7)	−0.2156 (9)	0.3653 (17)
H(1)	0.785^c	0.4081	0.4414
H(2)	0.0422	0.1222	0.3103
H(3)	0.1547	0.1109	0.2568
H(4)	0.1487	−0.0056	0.2404
H(5)	0.2996	0.0022	0.4399
H(6)	0.3607	0.0178	0.3026
H(7)	0.3315	0.1580	0.4257
H(8)	0.3494	0.1129	0.6088
H(9)	0.5139	0.2932	0.1482
H(10)	0.4357	0.2504	0.1601
H(11)	0.4007	0.3817	0.2936
H(12)	0.4661	0.3332	0.3899
H(13)	0.2200	0.3600	0.2000
H(14)	0.2352	0.2700	0.0947
H(15)	0.2124	0.3717	0.0097

[a] The copper atom occupies the special position $x = 0.0, y = 0.0$, $z = 0.0$ and was not varied. [b] Estimated standard deviations are in parentheses. [c] Hydrogen atom parameters were not refined.

Table VI. Geometrical Parameters for $Ni(1,4,7\text{-}TTCN)_2(BF_4)_2$

Interatomic Distances, Å			
Ni–S(1)	2.377 (1)	S(2)–C(3)	1.809 (4)
Ni–S(2)	2.380 (1)	S(3)–C(4)	1.823 (3)
Ni–S(3)	2.400 (1)	S(3)–C(5)	1.810 (4)
S(1)–C(1)	1.821 (4)	C(1)–C(2)	1.523 (6)
S(1)–C(6)	1.823 (4)	C(3)–C(4)	1.525 (5)
S(2)–C(2)	1.820 (3)	C(5)–C(6)	1.523 (5)
Interatomic Angles, deg			
S(1)–Ni–S(2)	88.88 (5)	Ni–S(3)–C(4)	103.6 (2)
S(1)–Ni–S(3)	88.61 (5)	Ni–S(3)–C(5)	99.3 (2)
S(2)–Ni–S(3)	88.04 (5)	S(1)–C(1)–C(2)	115.9 (2)
S(1)–Ni–S(2)′	91.12 (5)	C(1)–S(1)–C(6)	104.3 (2)
S(1)–Ni–S(3)′	91.39 (5)	S(2)–C(2)–C(1)	112.1 (2)
S(2)–Ni–S(3)′	91.96 (5)	C(2)–S(2)–C(3)	102.8 (2)
Ni–S(1)–C(1)	99.3 (1)	S(3)–C(4)–C(3)	111.2 (3)
Ni–S(1)–C(6)	103.8 (1)	C(4)–S(3)–C(3)	102.8 (2)
Ni–S(2)–C(2)	103.9 (1)	S(1)–C(6)–C(5)	113.2 (2)
Ni–S(2)–C(3)	99.9 (2)		

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(20) (a) Rosen, W.; Busch, D. H. *J. Chem. Soc., Chem. Commun.*, **1969**, 148. (b) Rosen, W.; Busch, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 4694. (c) Rosen, W.; Busch, D. H. *Inorg. Chem.* **1970**, *9*, 262.

(21) Johnson, C. K. "ORTEP"; Oak Ridge National Laboratory: Oak Ridge, TN.

Table VII. Geometrical Parameters for $Co(1,4,7\text{-}TTCN)_2(BF_4)_2 \cdot 2CH_3NO_2$

Interatomic Distances, Å			
Co–S(1)	2.356 (6)	S(2)–C(3)	1.81 (2)
Co–S(2)	2.240 (7)	S(3)–C(4)	1.81 (2)
Co–S(3)	2.367 (5)	S(3)–C(5)	1.80 (2)
S(1)–C(1)	1.80 (2)	C(1)–C(2)	1.52 (3)
S(1)–C(6)	1.81 (2)	C(3)–C(4)	1.58 (3)
S(2)–C(2)	1.80 (2)	C(5)–C(6)	1.55 (3)
Interatomic Angles, deg			
S(1)–Co–S(2)	89 (2)	Co–S(3)–C(4)	103 (2)
S(1)–Co–S(3)	88 (2)	Co–S(3)–C(5)	101 (2)
S(2)–Co–S(3)	90 (2)	S(1)–C(1)–C(2)	113 (2)
S(1)–Co–S(2)′	91 (2)	C(1)–S(1)–C(6)	102 (2)
S(1)–Co–S(3)′	92 (2)	S(2)–C(2)–C(1)	113 (2)
S(2)–Co–S(3)′	90 (2)	C(2)–S(2)–C(3)	104 (2)
Co–S(1)–C(1)	100 (2)	S(3)–C(4)–C(3)	112 (2)
Co–S(1)–C(6)	105 (2)	C(4)–S(3)–C(5)	103 (2)
Co–S(2)–C(2)	106 (2)	S(1)–C(6)–C(5)	110 (2)
Co–S(2)–C(3)	104 (2)		

Table VIII. Geometrical Parameters for $Cu(1,4,7\text{-}TTCN)_2(BF_4)_2 \cdot 2CH_3CN$

Interatomic Distances, Å			
Cu–S(1)	2.419 (3)	S(2)–C(3)	1.82 (1)
Cu–S(2)	2.426 (3)	S(3)–C(4)	1.82 (1)
Cu–S(3)	2.459 (3)	S(3)–C(5)	1.82 (1)
S(1)–C(1)	1.82 (1)	C(1)–C(2)	1.52 (1)
S(1)–C(6)	1.83 (1)	C(3)–C(4)	1.49 (2)
S(2)–C(2)	1.809 (4)	C(5)–C(6)	1.51 (1)
Interatomic Angles, deg			
S(1)–Cu–S(2)	88.1 (2)	Cu–S(3)–C(4)	102.6 (4)
S(1)–Cu–S(3)	88.0 (2)	Cu–S(3)–C(5)	97.5 (4)
S(2)–Cu–S(3)	87.2 (2)	S(1)–C(1)–C(2)	115.0 (7)
S(1)–Cu–S(2)′	91.9 (2)	C(1)–S(1)–C(6)	104.0 (5)
S(1)–Cu–S(3)′	92.0 (2)	S(2)–C(2)–C(1)	113.6 (7)
S(2)–Cu–S(3)′	92.8 (2)	C(2)–S(2)–C(3)	103.6 (5)
Cu–S(1)–C(1)	98.6 (4)	S(3)–C(4)–C(3)	112.6 (7)
Cu–S(1)–C(6)	103.2 (4)	C(4)–S(3)–C(5)	103.3 (5)
Cu–S(2)–C(2)	102.7 (4)	S(1)–C(6)–C(5)	112.4 (7)
Cu–S(2)–C(3)	98.9 (4)		

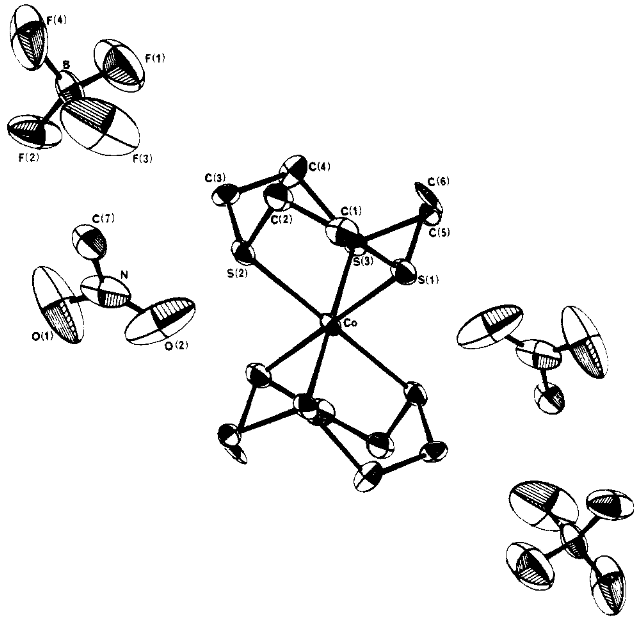

Figure 2. ORTEP[19] perspective drawing of $Co(1,4,7\text{-}TTCN)_2(BF_4)_2 \cdot 2CH_3NO_2$. The hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn to enclose 30% of the probability distribution.

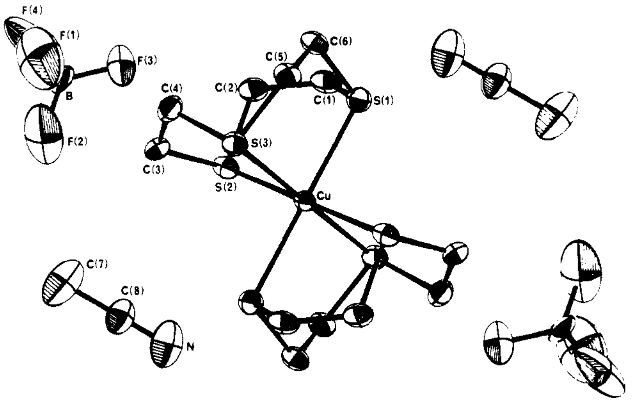

Figure 3. ORTEP[19] perspective drawing of $Cu(1,4,7\text{-}TTCN)_2(BF_4)_2 \cdot 2CH_3CN$. The hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn to enclose 30% of the probability distribution.

Table IX. Comparison of the Structural Features of Nickel(II) Complexes of Cyclic Thioethers

parameter (av)	$Ni(1,4,8,11\text{-}TTCT)(BF_4)_2$	$Ni(1,5\text{-}DTCO)_2Cl_2$	$Ni(1,4,7\text{-}TTCN)_2(BF_4)_2$
Ni-S, Å	2.176 (1)	2.49 (1)	2.386 (9)
S-C, Å	1.81 (1)	1.81 (2)	1.818 (9)
S-Ni-S, deg	89.7 (1), 90.3 (1)	88.8 (1), 91.2 (1)	88.5 (5), 91.5 (5)
Ni-S-C, deg	105 (3)	110 (3)	101 (2)
S-C-C, deg	109 (2)	119 (4)	113 (2)
C-S-C, deg	102.7 (3)	103 (1)	103 (1)

angles for sulfur atoms of different 1,4,7-TTCN molecules average 91.5°, only slightly deviating from regular octahedral coordination of 90°.[22] A comparison of the structural features of the free ligand and the complexed ligand indicates that there is relatively little distortion of the ligand upon complexation.[23]

The conformation adopted by 1,4,7-TTCN renders it chiral. Thus in these metal–bis(ligand) complexes, the $[M(1,4,7\text{-}TTCN)_2]$ unit may be the meso or *dl* diastereomer. In each of the cases which we have studied, the metal is at an inversion center; therefore, the two coordinated ligands must be of the opposite enantiomeric series, i.e., the complex is the meso diastereomer.

Nickel(II) complexes of macrocyclic[20,24] as well as mesocyclic[25] polythioethers have previously been prepared. However, the structure of only two of these have been characterized by X-ray crystallographic methods. In the square-planar complex (1,4,8,11-tetrathiacyclotetradecane)nickel(II) tetrafluoroborate, $[Ni(1,4,8,11\text{-}TTCT](BF_4)_2$,[6] the macrocycle serves as an encircling tetradentate ligand. In the six-coordinate complex bis(1,5-dithiacyclooctane)nickel(II) chloride, $[Ni(1,5\text{-}DTCO)_2]Cl_2$,[25b] the mesocyclic dithioether serves as a bridging monodentate ligand for two different metal atoms. Each nickel atom of the complex has four sulfur atoms arranged in a square around the metal center, with two chlorine

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(22) Surprisingly, the M–S bond lengths in these complexes increase in the order Co < Ni < Cu, whereas ionic radii increase in the order Ni(II) < Cu(II) < Co(II): Cotton, F. A.; Wilkinson, G., "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 14. The reason for the unusual order of M–S bond lengths is under investigation.

(23) The only significant geometric changes for the ligand on complexation are that the S–C–C–S torsion angle decreases (58.5, 52 (3), 51 (3), and 55 (1)° for the free ligand and for the Ni, Co, and Cu complexes, respectively), the C–C–S–C torsion angle increases (55.1, 61 (1), 64 (3), and 58 (1)° for the free ligand and for the Ni, Co, and Cu complexes, respectively), and the S···S nonbonded distances decrease (3.451 (2), 3.334 (3), 3.26 (2), and 3.38 (1) Å for the free ligand and for the Ni, Co, and Cu complexes, respectively).

(24) Black, D. St. C.; McLean, I. A. *Tetrahedron Lett.* **1969**, 3961.

(25) (a) Musker, W. K.; Hill, N. L. *Inorg. Chem.* **1972**, *11*, 710. (b) Hill, N. L.; Hope, H. *Ibid.* **1974**, *13*, 2079.

Table X. Comparison of Structural Features of Cobalt(II) Complexes of Thioethers

parameter (av)	$Co(2,5\text{-}DTH)_2(ClO_4)_2$	$Co(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3NO_2$
Co–S, Å	2.29 (1)	2.30 (8)
S–C, Å	1.84 (3)	1.82 (2)
S–Co–S, deg	88.1 (5), 91.9 (5)	88 (1), 92 (1)
Co–S–C, deg	100 (2)	104 (6)
S–C–C	116 (3)	112 (6)
C–S–C	101 (1)	101 (4)

Table XI. Comparison of Structural Features of Copper(II) Complexes of Cyclic Thioethers

parameter (av)	$Cu(1,4,8,11\text{-}TTCT)(ClO_4)_2$	$Cu(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3CN$
Cu–S, Å	2.303 (5)	2.423 (4), 2.459 (3)
S–C, Å	1.828 (5)	1.82 (1)
S–Cu–S, deg	89.9 (4), 90.1 (4)	87.8 (6), 92.2 (6)
Cu–S–C, deg	102 (3)	102.9 (4)
S–C–C, deg	109 (2)	112.9 (7)
C–S–C, deg		103.6 (5)

atoms occupying the apical positions of the bipyramid. A comparison of the structural features of these complexes with $[Ni(1,4,7\text{-}TTCN)_2](BF_4)_2$ is shown in Table IX. The Ni–S bond distances for $[Ni(1,4,7\text{-}TTCN)_2](BF_4)_2$ are longer than those observed in the square-planar complex $[Ni(1,4,8,11\text{-}TTCT)](BF_4)_2$ but shorter than those for the six-coordinate complex $Ni(1,5\text{-}DTCO)_2Cl_2$.

The only cobalt(II) complex of a cyclic polythioether previously reported is that of 1,4,7,10,13,16-hexathiaoctadecane.[24] Although its structure has not been studied by X-ray techniques, the structure of bis(2,5-dithiahexane)cobalt(II) perchlorate, $Co(2,5\text{-}DTH)_2(ClO_4)_2$, has been so studied.[26] In $Co(2,5\text{-}DTH)_2(ClO_4)_2$ the bidentate ligand coordinates the metal atom to give a rectangular arrangement of sulfur atoms. The two perchlorate ions serve as apical ligands to form a tetragonal bipyramid. The corresponding structural features of this distorted octahedral complex and $[Co(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3NO_2$ such as metal–sulfur bond lengths are very comparable as shown in Table X.

Copper(II) complexes of a macrocyclic[2] as well as a mesocyclic polythioether[27] have been previously prepared. An X-ray crystal structure of only the 1,4,8,11-tetrathiacyclotetradecane complex $Cu(1,4,8,11\text{-}TTCT)(ClO_4)_2$ has been reported,[2] but there have been numerous crystal structure studies on acyclic thioether complexes with copper(II).[28] In $Cu(1,4,8,11\text{-}TTCT)(ClO_4)_2$ the macrocyclic polythioether serves as an encircling tetradentate ligand as in the analogous nickel(II) complex. A comparison of the structural features of this complex with $[Cu(1,4,7\text{-}TTCN)_2](BF_4)_2\cdot 2CH_3CN$ is shown in Table XI. The geometry about the copper atom in $Cu(1,4,8,11\text{-}TTCT)(ClO_4)_2$, as in most six-coordinate copper(II) complexes, is severely distorted from octahedral owing to Jahn–Teller effects.[29] However, there is relatively little tetragonal distortion from octahedral geometry about the copper atom in $Cu(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3CN$. The Cu–S bond lengths in this complex vary only 0.040 Å (13 standard deviations) from the shortest to the longest. Substantial tetragonal distortion in this complex is apparently precluded by the geometrical requirements of the tridentate ligand. Such distortion would result in considerable strain in the ligand molecule.[30]

Like the bis complexes of 1,4,7-TTCN reported in this paper, the bis complexes of the tridentate ligand 1,4,7-triazacyclononane (1,4,7-TACN) and related ligands are postulated to have octahedral geometries about the metal atom. Six-coordinate octahedral structure has been suggested for bis(1,4,7-triazacyclononane)cobalt(III) bromide, $[Co(1,4,7\text{-}TACN)_2]Br_3$,[31] as well as bis[(*R*)-2-methyl-1,4,7-triazacyclononane]cobalt(III) iodide.[32] Analogous nickel(II)[33] and copper(II)[33,34] complexes have also been suggested to have octahedral coordination geometries.

Acknowledgment. The authors gratefully acknowledge support of this work by the National Institutes of Health, Grant No. HL 15104.

Registry No. 1,4,7-TTCN, 6573-11-1; $Ni(1,4,7\text{-}TTCN)_2(BF_4)_2$, 83650-36-6; $Co(1,4,7\text{-}TTCN)_2(BF_4)_2$, 83650-38-8; $Cu(1,4,7\text{-}TTCN)_2(BF_4)_2$, 83650-40-2; $Co(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3NO_2$, 83650-41-3; $Cu(1,4,7\text{-}TTCN)_2(BF_4)_2\cdot 2CH_3CN$, 83650-42-4; benzyltrimethylammonium methoxide, 122-08-7; bis(2-mercaptoethyl) sulfide, 3570-55-6; 1,2-dichloroethane, 107-06-2.

Supplementary Material Available: Tables of thermal parameters, additional geometrical parameters, a comparison of the structure of free 1,4,7-TTCN and complexed ligand, and structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

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(30) This conclusion must be tempered with a caveat: X-ray diffraction at room temperature may show a time-averaged octahedral structure about Cu in this complex but faster methods may reveal tetragonal distortion. See: Reedijk, J. *Transition Met. Chem.* **1981**, *6*, 195 and references therein.

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