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Combining Thiacyclophane and Benzocrown Ether Binding Sites in the Design of Haptoselective Ligands and Metalloreceptors

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ABSTRACT: Bis crown ether molecules containing separate S and O donor sets are synthesized in two steps from commercially available benzocrown ethers. Double bromomethylation of the aromatic ring followed by S-C bond formation in a Cs^+ mediated cyclization reaction produces ditopic macrocycles containing crown thioether and crown ether binding sites separated by a common benzene ring. These potential ligands display haptoselectivity, simultaneously coordinating a transition metal ion (Cu^+) through S-donors and an alkali metal ion (Na^+, K^+) in the O-donor set.. X-ray crystallographic and NMR data verify the nature of the cation binding selectivity. The resulting complexes demonstrate the potential to bind a substrate molecule (AMP^-) between the two metal centres (Cu^+ and Na^+).

INTRODUCTION

Ditopic molecules containing binding sites that are independently selective for different metal ions are termed *haptoselective*.[1] A number of these systems contain binding sites that are geometrically disposed for cooperative substrate binding.[2-12] Interestingly, a simple design that has received almost no attention is the combination of a crown thioether and a crown ether in a bis(macrocycle). Herein, we describe the synthesis and utility of two heteroditopic bis(macrocycles), **1** and **2**, which contain a crown thioether (S_3) and a crown ether (O_5 or O_6) binding site separated by a common benzene ring. A bis(macrocycle), similar to **1**, with separate *o*-xylyl-S_4 and benzocrown-O_5 macrocycles is known and although complexation with Co^{2+} and Na^+ were studied no substrate binding or structural data were reported.[12]

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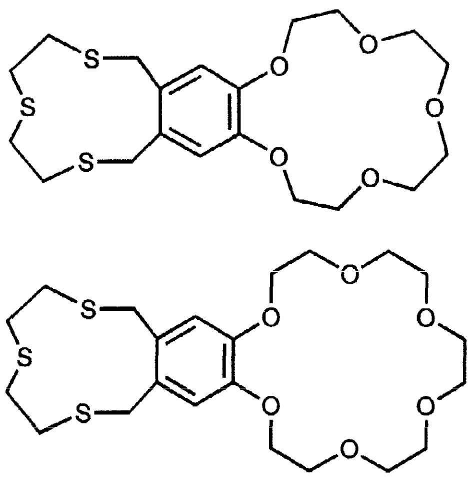
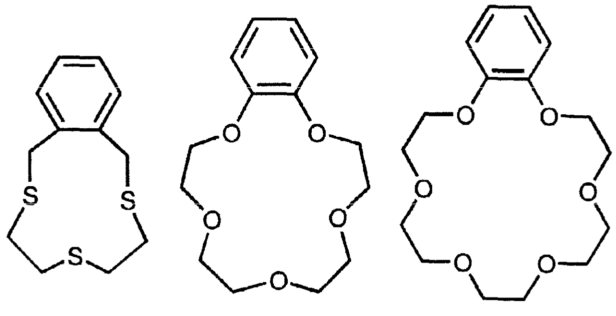


Scheme 1. Heteroditopic ligands **1** and **2** containing 5 and 6 O atoms respectively.

The thiacyclophane 2,5,8-trithia[9]-*o*-cyclophane, TT[9]OC, is known to coordinate transition metals in tetrahedral and octahedral geometries through an S_3 facial bonding mode,[13] while benzo-18-crown-6 ether and benzo-15-crown-5 ether bind alkali metal ions with the 15-membered ring favouring Na^+ and the 18-membered ring preferring K^+.[14]

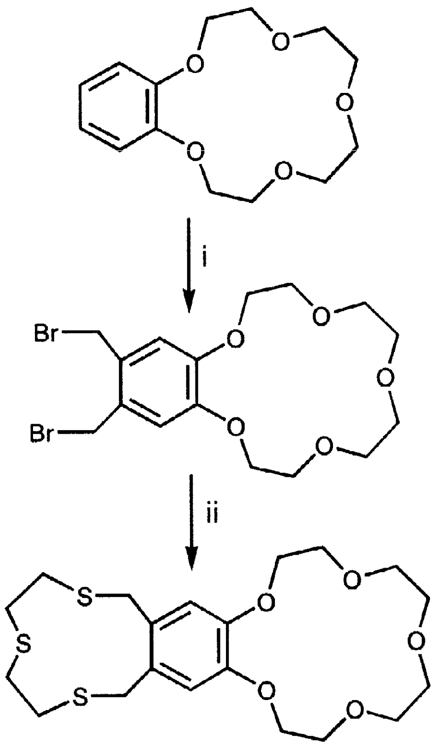


Scheme 2. From left to right: TT[9]OC, benzo-15-crown-5 ether, benzo-18-crown-6 ether.

Important in the design of these new bis(macrocycles) is the fact that the three thioether atoms coordinate transition metals leaving one of the ancillary ligands positioned over the face of the aromatic ring.[13] This means that for complexes of **1** or **2** a bound substrate would be directed towards the crown ether ring favouring interaction of a substrate molecule with *both* coordinated metal ions. This strategy therefore, combines crown thioether and crown ether binding sites in close proximity and provides the potential for cooperative binding of a substrate molecule *between* the two sites.

RESULTS AND DISCUSSION

The target heteroditopic ligands **1** and **2** were prepared as outlined in Scheme 3 for **1**. Bromomethylation of the benzocrown ether was achieved using a variation of the literature[15] method to give the 4,5-bis(bromomethyl)benzocrown ethers in 67 and 54% yield respectively. Formation of the crown thioether ring is mediated by Cs^+ in DMF[16] and provides the ligands **1** and **2** in reasonable yields of 73 and 65% respectively.



Scheme 3. *Reagents and conditions:* i, paraformaldehyde, glacial acetic acid, 40% HBr, 2 days, 5°C, 67%. ii, (HSCH$_2$CH$_2$)$_2$S, Cs$_2$CO$_3$, DMF, 55°C, 2 days, 73%.

The reaction of **1** and **2** with CuI in MeCN solution gave the complexes [CuI(**1**)] and [CuI(**2**)]. The X-ray crystal structure of [CuI(**1**)] was determined and an ORTEP drawing is shown in Figure 1.[17]

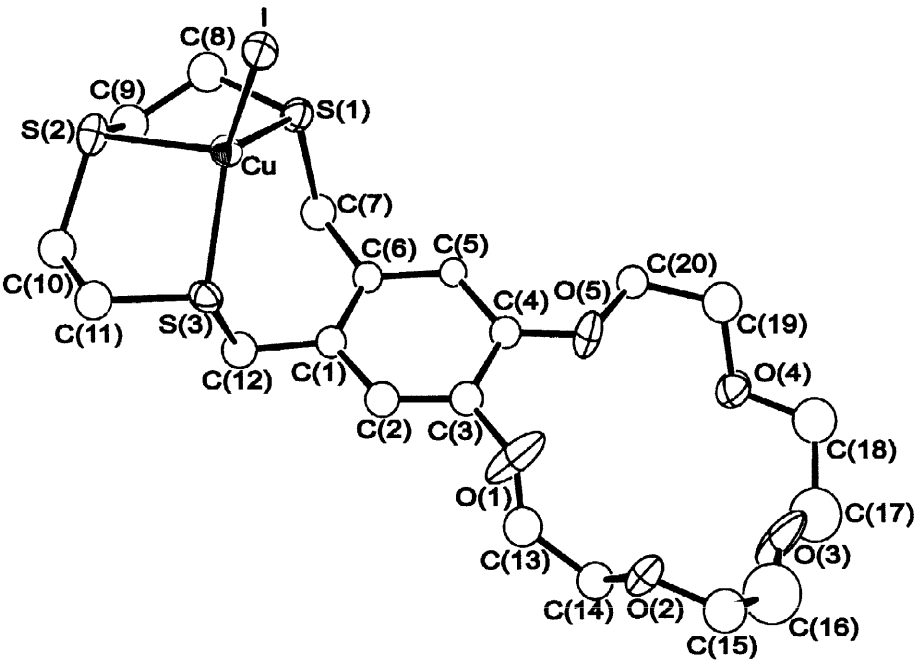


Figure 1. ORTEP drawing of [CuI(**1**)] showing the atom numbering scheme. Some significant bonding parameters are: Cu-I 2.530(2), Cu-S(1) 2.300(5), Cu-S(2) 2.389(5), Cu-S(3) 2.291(5) Å, I-Cu-S(1) 112.8(1), I-Cu-S(2) 117.0(1), I-Cu-S(3) 120.0(1), S(1)-Cu-S(2) 93.5(2), S(1)-Cu-S(3) 116.1(2), S(2)-Cu-S(3) 92.6(2)°.

Addition of NaI and KI to solutions of [CuI(**1**)] and [CuI(**2**)] respectively, showed chemical shift changes (Table 1) for the crown ether methylene protons indicative of alkali metal binding.[14] This verifies that the ligands will act in a ditopic fashion, simultaneously binding a Cu(I) ion via sulfur donors and an alkali metal ion via ether oxygen atoms.In order to demonstrate metal ion haptoselectivity and cooperative binding of a biologically relevant substrate, equimolar amounts of $[Cu(MeCN)_4][ClO_4]$, **1** and NaAMP were combined in CD_3CN/D_2O (98:2 v/v) and the ^1H NMR spectrum recorded. Since NaAMP is not particularly soluble in this solvent mixture, the formation of a homogenous solution upon mixing these reagents was taken as a positive indication of substrate-complex interaction. Chemical shift changes for the SCH_2 and OCH_2 protons were very similar to those observed previously for Cu(I) and Na^+ coordination to **1**. Upon coordination of **1** to Cu(I), the benzylic protons changed from a singlet to an AB quartet at δ 3.84 ppm and SCH_2CH_2 protons split from a multiplet centered at 2.65 ppm to a pair of multiplets at δ 3.34 and 2.83 ppm. Binding of Na^+ to the crown ether portion results in peak broadening and a shift in the ethyleneoxy proton resonances ranging from $\Delta\delta$ 0.09 to 0.13 ppm. Additionally, chemical shifts for the adenine nucleobase were consistent with coordination to Cu(I) at N7;[18] H8 $\Delta\delta = 0.14$, H2 $\Delta\delta = 0.05$. It should also be noted that when this experiment was conducted in the absence of Cu(I) ions the mixture remained heterogeneous, suggesting coordination of AMP^- to the transition metal center is a necessary step for dissolution. Figure 2 shows the results of a molecular modeling study (see experimental) and illustrates a possible *intramolecular* binding mode in which AMP^- bridges between the two metal binding sites. Unfortunately, similar experiments with ADP and ATP salts were hampered by poor solubility.[19] Thus no selectivity or comparative data are yet available for this system.

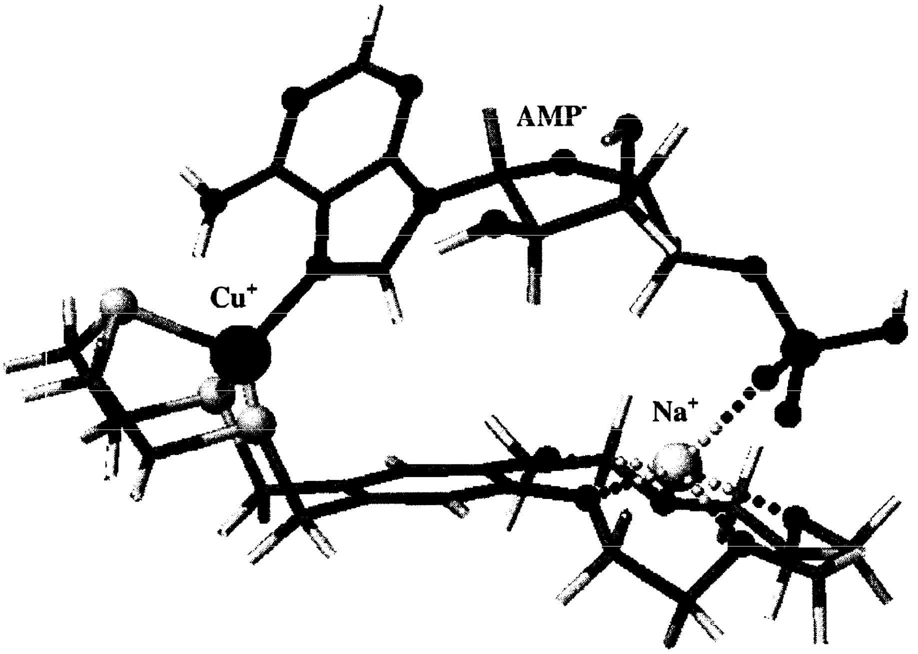


Figure 2. A ball-and-stick framework model of $[Cu(\mathbf{1})(AMP)(Na)]^+$ illustrating the potential intramolecular receptor-substrate interaction proposed by molecular modeling .

Ligands **1** and **2** are rare examples of bis(macrocycles) with separate crown thioether and crown ether donor sets. Haptoselectivity was demonstrated by simultaneously binding Cu(I) to the thioether site and Na^+ to the ether site. Solution observations are consistent with the formation of a species of the type $[Cu(\mathbf{1})(AMP)(Na)]^+$ in which the bimetallic complex acts as a ditopic metalloreceptor for the AMP^- ion.

ACKNOWLEDGMENTS

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EXPERIMENTAL

General: $[Cu(MeCN)_4][ClO_4]$ was prepared by the literature method.[20] All materials were purchased from Aldrich, except AMP sodium salt which was purchased from Sigma. All reactions were carried out under an atmosphere of dry $N_2(g)$ using standard Schlenk techniques and all solvents were dried, distilled and degassed prior to use. ^1H and ^{13}C NMR spectra were recorded on a Brüker AC300 NMR spectrometer locked to the deuterated solvent. Mass spectrometry was performed on a Kratos Profile instrument. Elemental analyses were performed by Canadian Microanalytical Services, Delta, British Columbia, Canada.

Preparation of 4,5-Bis(bromomethyl)benzo-15-crown-5 ether: *Note*: care must be taken not to warm the mixture during reaction or work-up as this drastically reduces the yield. Benzo-15-crown-5 ether (0.996 g, 3.60 mmol) and paraformaldehyde (0.530 g, 17.6 mmol) were placed in a stoppered 50 mL Erlenmeyer flask. A mixture of glacial acetic acid (15.2 mL) and 40% HBr (5.15 mL) was added to the flask and the contents stirred at 5°C. After 2 days, the solution turned dark green. The solvent was removed under vacuum at a temperature not exceeding 40°C. The resulting black residue was dissolved in THF (30 mL) and *n*-hexane added until the solution became cloudy. A dark green oil separated from the solution. The oil was discarded and the resulting pale beige solution evaporated to dryness. The resulting off-white solid was recrystallized from CH_2Cl_2. Yield 1.097 g (67%). ^1H NMR ($CDCl_3$): δ(ppm) 6.82 (s, 2H, Ar), 4.58 (s, 4H, Bz), 4.12 (t, 4H, OCH_2), 3.88 (t, 4H, OCH_2), 3.72 (m, 8H, OCH_2CH_2O). ^{13}C NMR ($CDCl_3$): δ(ppm) 149.53 129.44, 116.08 (Ar), 71.14, 70.47, 69.40, 69.08 (OCH_2), 30.54 (Bz). EI-MS (m/z): $[M]^+ = 454$.

Preparation of 4,5-Bis(bromomethyl)benzo-18-crown-6 ether: *Note*: care must be taken not to warm the mixture during reaction or work-up as this drastically reduces the yield. Benzo-16-crown-6 ether (1.126 g, 3.60 mmol) and paraformaldehyde (0.530 g, 17.6 mmol) were placed in a stoppered 50 mL Erlenmeyer flask. A mixture of glacial acetic acid (15.6 mL) and 40% HBr (5.15 mL) was added to the flask and the contents stirred at 5°C. After 2 days, the solution turned light yellow. The solvent was removed under vacuum at a temperature not exceeding 50°C. The resulting beige solid was stirred with CH_2Cl_2 for 1h. Any undissolved solid was filtered and discarded. The filtrate was evaporated to dryness and the resulting residue recrystallized from CH_2Cl_2 to yield a white solid. Yield 0.978 g (54%). ^1H NMR ($CDCl_3$): δ(ppm) 6.82 (s, 2H, Ar), 4.58 (s, 4H, Bz), 4.15 (t, 4H, OCH_2), 3.90 (t, 4H, OCH_2), 3.73 (m, 4H, OCH_2), 3.69 (m, 4H, OCH_2), 3.66 (s, 4H, OCH_2). ^{13}C NMR ($CDCl_3$): δ(ppm) 148.16 129.25, 115.78 (Ar), 70.85, 70.70, 70.57, 69.33, 68.97 (OCH_2), 31.48 (Bz). EI-MS (m/z): $[M]^+ = 498$.

Preparation of 1: A solution of 4,5-bis(bromomethyl)benzo-15-crown-5 ether (1.097 g, 2.42 mmol) and 2-mercaptoethyl sulfide (0.373 g, 2.42 mmol) in DMF (200 mL) was added, via constant addition funnel, to a stirred suspension of Cs_2CO_3 (1.577 g, 4.83 mmol) in DMF (500 mL) at 55°C over 2 days. The DMF was removed under vacuum and the resulting orange residue extracted with CH_2Cl_2. After filtration, the organic solution was washed with 0.1 *M* NaOH (2 x 100 mL) and distilled water (2 x 100 mL) and dried over anhydrous $MgSO_4$. Addition of *n*-hexane to the CH_2Cl_2 solution resulted in precipitation of a white solid. Colourless crystalline material was obtained by slow evaporation of a CH_2Cl_2 solution of the compound. Yield

0.789 g (73%). ^{1}H NMR (CD_3CN): δ(ppm) 7.06 (s, 2H, Ar), 4.05 (t, OCH_2, 4H), 3.84 (s, 4H, Bz), 3.77 (t, 4H, OCH_2), 3.62 (m, 8H, OCH_2CH_2O), 2.65 (m, 8H, SCH_2CH_2S). ^{13}C NMR (CD_3CN): δ(ppm) 147.67 130.99, 114.68 (Ar), 71.43, 70.82, 69.90, 69.55 (OCH_2), 37.47 (Bz), 32.67, 32.20 (SCH_2). LSI-MS (m/z): $[M+H]^+$ = 446. Anal. Calcd. for $C_{20}H_{30}S_3O_5$: C, 53.77; H, 6.78; S, 21.54. Found: C, 53.24; H, 6.43; S, 21.45.

Preparation of 2: A solution of 4,5-bis(bromomethyl)benzo-18-crown-6 ether (1.756 g, 3.52 mmol) and 2-mercaptoethyl sulfide (0.544 g, 3.52 mmol) in DMF (200 mL) was added, via constant addition funnel, to a stirred suspension of Cs_2CO_3 (2.297 g, 7.05 mmol) in DMF (500 mL) at 55°C over 2 days. The DMF was removed under vacuum and the resulting orange residue extracted with CH_2Cl_2. After filtration, the organic solution was washed with 0.1 *M* NaOH (2 x 100 mL) and distilled water (2 x 100 mL) and dried over anhydrous $MgSO_4$. Addition of *n*-hexane to the CH_2Cl_2 solution and refrigeration resulted in precipitation of a white solid. Yield 1.123 g (65%). ^{1}H NMR (CD_3CN): δ(ppm) 7.06 (s, 2H, Ar), 4.11 (t, OCH_2, 4H), 3.84 (s, 4H, Bz), 3.72 (t, 4H, OCH_2), 3.57 (m, 4H, OCH_2), 3.56 (m, 4H, OCH_2), 3.53 (s, 4H, OCH_2), 2.64 (m, 8H, SCH_2CH_2S). ^{13}C NMR (CD_3CN): δ(ppm) 148.36 130.38, 114.20 (Ar), 71.02, 71.01, 71.00 69.72, 68.69 (OCH_2), 37.45 (Bz), 32.61, 32.19 (SCH_2). LSI-MS (m/z): $[M+H]^+$ = 491. Anal. Calcd. for $C_{22}H_{34}S_3O_6$: C, 53.84; H, 7.00; S, 19.60. Found: C, 53.33; H, 6.81; S, 19.90.

Preparation of [CuI(1)]: **1** (0.100 g, 0.22 mmol) was dissolved in a solution of CH_2Cl_2 (7.0 mL) and MeCN (7.0 mL). CuI (0.0426 g, 0.22 mmol) was added and the solution stirred at reflux, in the dark, for 4 h. The solution was filtered hot and the solvent removed to yield a light beige solid. Crystalline material was obtained by slow evaporation of an MeCN solution of the product. Yield 0.142 g (95%). ^{1}H NMR (CD_3CN, 235 K): δ(ppm) 6.90 (s, 2H, Ar), 4.14 (m, OCH_2, 4H), 3.88 (d, 2H, J = 11.1 Hz, Bz), 3.78 (d, 2H, J = 11.1 Hz, Bz), 3.56 (m, 12H, OCH_2), 3.40 (m, 4H, SCH_2), 2.74 (m, 4H, SCH_2CH_2S). ^{13}C NMR (CD_3CN, 235 K): δ(ppm) 149.05 127.45, 114.18 (Ar), 70.52, 69.85, 68.64 68.39, (OCH_2), 37.11 (Bz), 35.79, 35.22 (SCH_2). LSI-MS (m/z): $[M-I]^+$ = 509. Anal. Calcd. for $C_{20}H_{30}CuIS_3O_5$: C, 37.70; H, 4.76. Found: C, 37.55; H, 4.62.

Preparation of [CuI(2)]: **2** (0.225 g, 0.46 mmol) was dissolved in a solution of CH_2Cl_2 (10 mL) and MeCN (10 mL). CuI (0.0873 g, 0.46 mmol) was added and the solution stirred at reflux, in the dark, for 4 h. The solution was filtered hot and allowed to evaporate slowly to give colourless crystalline material. Yield 0.310 g (99%). ^{1}H NMR (CD_3CN, 235 K): δ(ppm) 6.93 (s, 2H, Ar), 4.14 (s, br OCH_2, 4H), 3.88 (d, 2H, J = 11.2 Hz, Bz), 3.78 (d, 2H, J = 11.2 Hz, Bz), 3.70-3.50 (m, 16H, OCH_2), 3.41 (d, 4H, SCH_2), 2.76 (m, 4H, SCH_2CH_2S). ^{13}C NMR (CD_3CN, 235 K): δ(ppm) 146.78 127.51, 114.14 (Ar), 71.50, 70.66, 69.66, 69.53 68.30, (OCH_2), 37.28 (Bz), 35.72, 35.23 (SCH_2). LSI-MS (m/z): $[M-I]^+$ = 553. Anal. Calcd. for $C_{22}H_{34}CuIS_3O_6$: C, 38.83; H, 5.05. Found: C, 38.77; H, 5.00.

Reaction of CuI Complexes with MI (M = Na^+ or K^+): In a typical reaction, an equivalent of [CuI(1)] or [CuI(2)] (*ca.* 25 mg) was added to MeCN (7.0 mL) and heated until all the solid was dissolved; usually less than 5 min. An equivalent of MI was added and the solution refluxed for 5 min. The solution was filtered hot, cooled and diethyl ether added until the solution became cloudy. The capped container was then refrigerated for 12 h to precipitate a white solid. Yields were usually >90%. ^{1}H NMR spectra were recorded to determine whether the alkali cation was coordinated to the crown ether. These results are summarized in Table 1. Attempts to obtain analytically pure material for analysis or X-ray structure determination have failed to date.

Reaction of [Cu(1)(MeCN)][ClO$_4$] with NaAMP: *Caution! Perchlorate salts of metal complexes with organic ligands can be explosive.* [Cu(MeCN)$_4$][ClO$_4$] (0.0147 g, 0.045 mmol) and **1** (0.0200 g, 0.045 mmol) were dissolved in CD$_3$CN (1.0 mL) in an NMR tube and sonicated at room temperature for 5 min. NaAMP (0.0165 g, 0.045 mmol) and D$_2$O (1 drop) were added and the sonicated stirred for a further 5 min. The ^{1}H NMR spectrum was recorded immediately. Oxidation to Cu(II) was evident after approximately 30 min as evidenced by formation of a greenish tinge to the solution. No pure solid samples could be isolated. ^{1}H NMR (CD$_3$CN/D$_2$O): δ(ppm) 8.48 (s, 1H, AMP-H8), 8.12 (s, br, 1H, AMP-H2), 6.91 (s, 2H, Ar), 6.00 (s, br, 2H, AMP-H1') 4.58 (s, 1H, sugar), 4.40 (s, 1H, sugar), 4.07 (s, 4H, OCH$_2$ & 1H, sugar), 3.99 (s, 4H, Bz & 2H, sugar-CH$_2$), 3.79 (s, 4H, OCH$_2$), 3.61 (m, 4H, OCH$_2$), 3.50 (s, 4H, OCH$_2$), 2.85 (m, 8H, SCH$_2$).

Molecular Modeling: Molecular modeling studies of the interaction of [Cu(**1**)(MeCN)][ClO$_4$] with NaAMP was carried out using standard molecular mechanics (MMX) employing CAChe Scientific Inc. software (version 3.7) running on an Apple Power Macintosh 7100/66.

X-ray Diffraction Study: Diffraction experiments were performed on a four-circle Rigaku AFC6S diffractometer with graphite-monochromatized MoKα radiation. The unit cell constants and orientation matrix for data collection were obtained from 25 centered reflections ($15^\circ < 2\theta < 35^\circ$). Machine parameters, crystal data and data collection parameters are summarized in Table 2. The intensities of three standard reflections were recorded every 150 reflections and showed no statistically significant changes over the duration of the data collection. The intensity data were collected using a ω–2θ scan technique, in four shells ($2\theta < 30$, 40, 45 and 50°). Absorption coefficients were calculated and an empirical absorption correction was applied to the data. The data were processed using the teXsan software package[21] running on an SGI Challenge XL computer. Refinements were carried out using full-matrix least-squares techniques on F by minimizing the function $\Sigma w(F_o\text{-}F_c)^2$, where $w = 1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors[22] and anomalous dispersion terms[23,24] were taken from the usual sources. In the final cycles of refinement, all non-hydrogen and non-carbon atoms were assigned anisotropic thermal parameters. Fixed hydrogen atom contributions were included with thermal parameters 1.2 times the isotropic thermal parameter of the attached carbon atom and were updated after each refinement. Colourless crystals of [CuI(1)] were grown by slow evaporation of an MeCN solution of the compound. A statistical analysis of the intensity distributions and a determination of the observed extinctions were consistent with the space group *C2/c* and this was confirmed by a successful solution refinement. A total of 5192 reflections were collected and 1500 reflections with $F_o > 3\sigma(F_o)^2$ were used in the refinement. Positions of the copper, iodine and sulfur atoms were determined by direct methods from the E-map with the highest figure-of-merit and the remaining atoms located from successive difference Fourier calculations. In the final cycles of refinement, the iodine, copper, sulfur and oxygen atoms were assigned anisotropic thermal parameters. The crown ether macrocycle exhibited two-fold disorder for the linkage (O(4)-C(19)-C(20)-O(5)). This was modeled by defining two sets of ethylene chains with site occupancies of 50%. All four carbon atoms were refined isotropically with individual thermal parameters. In addition, the central aromatic ring was refined as a rigid group with individual isotropic thermal parameters. This resulted in R = 4.04%, R_w = 5.03% and goodness-of-fit = 1.63 at convergence. The final Δ/σ value for any parameter was less than 0.002. A final difference Fourier map calculation showed no peaks of chemical significance; the largest was 0.69 electrons/Å^3 associated with O(3).[24]

Table 1. ^{1}H NMR Shifts[a] (CD_3CN) for the Reactions of [CuI(**1**)] and [CuI(**2**)] with NaI and KI.

CH_2 Group[b]	[CuI(**1**)]	[CuI(**2**)]	[CuI(**1**)(Na)]$^+$	[CuI(**2**)(Na)]$^+$	[CuI(**1**)(K)]$^+$	[CuI(**2**)(K)]$^+$
Ar	6.91	6.92	7.08	6.95	7.02	6.99
O1	4.08	4.14	4.21	4.13	4.20	4.17
O2	3.78	3.73	3.71	3.81	3.76	3.81
O3	3.62	3.59	3.69	3.61	3.71	3.63
O4	3.62	3.55	3.27	3.58	3.71	3.61
O5	-	3.53	-	3.54	-	3.57
S1	3.91	3.91	3.97	3.92	3.97	3.93
S2	3.34	3.27	~3.3	~3.3	3.22	~3.4
S3	2.83	2.82	2.64	2.76	2.64	2.69

[a] δ (ppm). [b] CH_2 groups are numbered out from the aromatic ring and designated S or O for the different crowns.

Table 2. Crystallographic data for [CuI(**1**)]•MeCN.

Formula	$C_{22}H_{33}CuINO_5S_3$
fw	678.14
a, Å	28.080(5)
b, Å	12.065(4)
c, Å	16.678(8)
β, °	104.35(2)
space group	*C2/c* (No. 15)
V, Å^3	5474(3)
ρ, g cm^{-3}	1.65
Z	8
μ, cm^{-1}	21.87
T, °C	25
goodness of fit	1.63
$R(F)$, % [a]	4.04
$Rw(F^2)$, % [b]	5.03

[a] $R(F) = \Sigma\Delta/\Sigma(Fo)$, $\Delta = |(Fo - Fc)|$, [b] $Rw(F^2) = \Sigma[w(Fo^2 - Fc^2)^2]$

Table 3. Selected Bond Distances and Angles for [CuI(**1**)].MeCN.

Bonded Atoms		Distance (Å)	Bonded Atoms		Distance (Å)
Cu(1)	I(1)	2.530(2)	O(1)	C(13)	1.08(6)
Cu(1)	S(1)	2.300(5)	O(2)	C(14)	1.31(4)
Cu(1)	S(2)	2.389(5)	O(2)	C(15)	1.40(2)
Cu(1)	S(3)	2.291(5)	O(3)	C(16)	1.08(3)
S(1)	C(7)	1.83(2)	O(3)	C(17)	1.34(3)
S(1)	C(8)	1.83(2)	O(4)	C(18)	1.41(2)
S(2)	C(9)	1.82(2)	O(4)	C(19)	1.42(2)
S(2)	C(10)	1.85(2)	O(5)	C(4)	1.33(2)
S(3)	C(11)	1.81(2)	O(5)	C(20)	1.39(2)
S(3)	C(12)	1.86(2)	N(1)	C(21)	1.11(2)
O(1)	C(3)	1.36(2)			

Bonded Atoms			Angle (°)	Bonded Atoms			Angle (°)
I(1)	Cu(1)	S(1)	112.8(1)	Cu(1)	S(3)	C(11)	99.2(6)
I(1)	Cu(1)	S(2)	117.0(1)	Cu(1)	S(3)	C(12)	104.6(5)
I(1)	Cu(1)	S(3)	120.0(1)	C(11)	S(3)	C(12)	102.3(7)
S(1)	Cu(1)	S(2)	93.5(2)	C(3)	O(1)	C(13)	138(4)
S(1)	Cu(1)	S(3)	116.1(2)	C(3)	O(1)	C(13a)	130(3)
S(2)	Cu(1)	S(3)	92.6(2)	C(13)	O(1)	C(13a)	89(4)
Cu(1)	S(1)	C(7)	110.8(6)	C(14)	O(2)	C(14a)	84(2)
Cu(1)	S(1)	C(8)	96.6(6)	C(14)	O(2)	C(15)	119(2)
C(7)	S(1)	C(8)	99.8(8)	C(14a)	O(2)	C(15)	115(2)
Cu(1)	S(2)	C(9)	97.0(6)	C(16)	O(3)	C(17)	141(3)
Cu(1)	S(2)	C(10)	98.3(6)	C(18)	O(4)	C(19)	112(1)
C(9)	S(2)	C(10)	104.2(8)	C(4)	O(5)	C(20)	121(1)

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