Heavy Metal Complexes of Oxa-Crowned Derivatives of Dithiomaleonitrile

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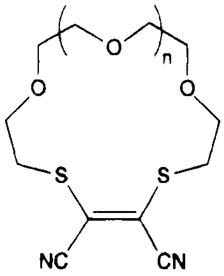
An improved synthesis of 1,4,7-trioxa-10,13-dithiacyclopentadec-11-en-11,12-dicarbonitrile, **2**, and 1,4,7,10-tetraoxa-13,16-dithiacyclooctadec-14-en-14,15-dicarbonitrile, **3**, and their coordination chemistry with Ag(I) are presented. The metal complexes have been investigated by X-ray structural and spectroscopic methods. The complex [**2**·Ag]BF_4, **6**, forms colorless crystals in the triclinic space group $P\bar{1}$ with unit cell parameters a = 8.020(4) Å, b = 16.032(5) Å, c = 16.116(7) Å, α = 116.62(2)°, β = 102.34(2)°, γ = 91.71(2)°, and Z = 4. The structure of **6** contains two unique, cocrystallized, 1:1 Ag complexes, a polymeric form and a discrete monomeric form. In both cases, the five macrocyclic donor atoms ligate the Ag(I) ion in an endocyclic fashion. The monomeric complex is further coordinated to a F atom from the BF_4 anion, while in the polymeric form the Ag(I)−macrocycle units are linked by the coordination of a nitrile N atom from a neighboring macrocycle. The complex [**3**·Ag]BF_4, **7**, crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell parameters a = 10.074(4) Å, b = 12.575(4) Å, c = 16.144(6) Å, and Z = 4. The structure of **7** is polymeric and consists of an endocyclic Ag(I) ion coordinated by three of the four macrocyclic O donor atoms and only one S atom. As in the polymer form of **6**, the links between Ag−macrocycle units are through the coordination of a nitrile N atom from a neighboring macrocycle. NMR (^{13}C) studies confirm that the complex persists in methanol solution, with an average structure that involves the coordination of all macrocyclic heteroatoms in both **6** and **7**.

Introduction

Macrocyclic ligands containing either sulfur or oxygen donor atoms have been extensively studied over the past 25 years. Thioether crowns are known to coordinate "soft" cations (low-valent transition metals and group Ib and IIb metals)[1] while purely oxygen-containing crowns are ideally suited for the ligation of "hard" cations (e.g. group I and II metals).[2] There has been considerably less effort directed toward the coordination properties of macrocycles having a mixed donor set of sulfur and oxygen heteroatoms.[3−6] In contrast to the purely S- or O-containing crowns, a mixed set of S and O donor atoms imparts a preference for the coordination of heavy metal ions at the expense of transition and alkali metal ions. Thus, oxathioether crowns have been exploited for their ability to extract and transport heavy metal ions.[3a,6,7]

We are specifically interested in oxa-crowned derivatives of dithiomaleonitrile (e.g. macrocycles **1**−**3**). The effects of the maleonitrile unit on the coordination chemistry of these macrocycles are not fully understood. In contrast to those in the saturated analogs (e.g. **4** and **5**),[8] the sulfur atoms in the uncomplexed macrocycles **1** and **2** have *restricted* exodentate conformations which should enhance the formation of endocyclic complexes.[9] However, the electron-withdrawing effect of the maleonitrile unit may reduce the donating ability of the macrocyclic S atoms.[10] We also note that, in addition to their utility as ligands, they are key precursors to crowned octakis(alkylthio)tetraazaporphyrins.[11]



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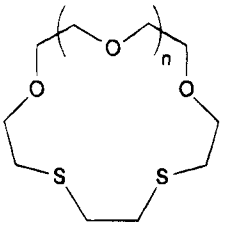
2 n = 1
3 n = 2



4 n = 1
5 n = 2

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Holdt recently described exocyclic PdX_2 (X = Cl, Br) complexes of the oxa-crowned dithiomaleonitrile derivatives **1** and **3**.[6] Each macrocycle coordinates the Pd(II) ion through the two S atoms alone in a fashion analogous to that observed for the Pd(II) complexes of the related fully saturated crowns 1,4-dithia-7,10,13-trioxacyclopentadecane,[3b] **4**, and 1,4-dithia-7,10,13,16-tetraoxacyclooctadecane, **5**.[4b] Holdt further observed a direct proportionality between extraction constants and stability constants for $PdCl_2$ and Ag(I) complexes of ligands **1**−**3**. All three macrocycles were more effective at the extraction of $PdCl_2$ than of Ag(I), with ligand **1** exhibiting the highest selectivity.

In a recent report on the complex of **3**·$HgCl_2$, we described the unique solid-state endocyclic coordination of the Hg(II) cation by only the macrocyclic O atoms.[10] The lack of S-coordination was surprising and contrary to previously reported oxathioether[5a,b] and thioether[12] crown complexes of $HgCl_2$. Indeed, in each of the $HgCl_2$ complexes with the related oxathioether crowns **5**[5b] and 1,4,13,16-tetraoxa-7,10-dithia[16](1,1′)ruthenocenophane,[5a] the Hg atom is tetrahedrally coordinated by two Cl atoms and two macrocyclic S atoms in an exocyclic fashion, without bonds to the O donor atoms of the crown. Presumably, the electron-withdrawing maleonitrile unit of **3** reduces the affinity of the S atoms for the Hg(II) ion.

This intriguing result led us to investigate the ability of **2** and **3** to ligate other metal ions in an *endocyclic* manner. Here, we report an improved general synthesis of crowned dithiomaleonitrile derivatives and provide spectroscopic and X-ray structural characterization of endocyclic Ag(I) complexes of ligands **2** and **3**.

Experimental Section

Materials and Apparatus. Disodium dithiomaleonitrile was prepared according to literature procedures.[13] All other reagents and solvents were of reagent grade quality and were obtained from commercial suppliers and used without further purification. Proton and carbon NMR spectra were recorded on a Varian Gemini-300 (300 MHz) spectrometer. Infrared spectra were recorded on a Mattson Instruments Alpha Centauri FTIR spectrometer. EI and FAB mass spectra were recorded using a VG-70-250SE instrument. Elemental analyses were performed by Searle.

Preparation of 1,4,7-Trioxa-10,13-dithiacyclopentadec-11-en-11,12-dicarbonitrile (2). A 1-L three-necked round-bottomed flask, charged with 550 mL of anhydrous DMF, was heated to 90 °C under a nitrogen atmosphere. Tetraethylene glycol di-*p*-toluenesulfonate (5.26 g; 10.5 mmol) in DMF (50 mL) and disodium dithiomaleonitrile (1.95 g; 10.5 mmol) were then simultaneously added to the DMF solution. The reaction was continued for 18−24 h, at which time the DMF was removed under reduced pressure. The golden-brown residue was taken up in chloroform and washed with water. The organic layer was separated from the mixture and dried with $MgSO_4$. Pure **2** (1.50 g) was isolated as a white crystalline solid following column chromatography on silica (1−2% $CH_3OH/CHCl_3$, eluent): yield 48%; mp 129−131 °C (lit.[14] 125−127 °C); ^1H NMR ($CDCl_3$) δ 3.31 (4 H, t, SCH_2), 3.60 (8 H, m, OCH_2), 3.71 (4 H, t, OCH_2); ^1H NMR (CD_3OD) δ 3.34 (4 H, t, SCH_2), 3.57 (8 H, s, OCH_2), 3.69 (4 H, t, OCH_2); ^{13}C NMR ($CDCl_3$) δ 34.83, 69.44, 70.02, 70.41, 112.59, 122.00; ^{13}C NMR (CD_3OD) δ 35.97, 71.30, 71.42, 71.57, 113.96, 123.47; EI MS *m*/*e* 300 (M^+); HR EI MS *m*/*e* 300.0597 (M^+) (calcd for $C_{12}H_{16}N_2O_3S_2$, *m*/*e* 300.0602).

Preparation of 1,4,7,10-Tetraoxa-13,16-dithiacyclooctadec-14-en-14,15-dicarbonitrile (3). Disodium dithiomaleonitrile (1.70 g; 9.15 mmol) was reacted with pentaethylene glycol di-*p*-toluenesulfonate (5.0 g; 9.15 mmol) by the method described for **2**. The product (1.1 g) was isolated as a yellowish crystalline solid: yield 35%; mp 62−65 °C (lit.[14] 64−66 °C); ^1H NMR ($CDCl_3$) δ 3.30 (4 H, t, SCH_2), 3.65 (8 H, m, OCH_2), 3.68 (4 H, s, OCH_2), 3.74 (4 H, t, OCH_2); ^1H NMR (CD_3OD) δ 3.22 (4 H, t, SCH_2), 3.54 (12 H, m, OCH_2), 3.62 (4 H, t, OCH_2); ^{13}C NMR ($CDCl_3$) δ 34.92, 69.40, 70.66, 70.88, 71.00, 112.33, 121.80; ^{13}C NMR (CD_3OD) δ 35.88, 71.08, 71.85, 71.98, 113.74, 123.28; FAB MS *m*/*e* 345 (M + H^+); EI MS *m*/*e* 344 (M^+); HR EI MS *m*/*e* 344.0861 (M^+) (calcd for $C_{14}H_{20}N_2O_4S_2$, *m*/*e* 344.0865).

Table 1. Crystallographic Data for Complexes **6** and **7**

	6	**7**
formula	$C_{12}H_{16}AgBF_4N_2O_3S_2$	$C_{14}H_{20}AgBF_4N_2O_4S_2$
mol wt	495.1	539.1
space group	$P\bar{1}$	$P2_12_12_1$
a/Å	8.020(4)	10.074(4)
b/Å	16.032(5)	12.575(4)
c/Å	16.116(7)	16.144(6)
α/deg	116.62(2)	
β/deg	102.34(2)	
γ/deg	91.71(2)	
V/Å^3	1790.9(12)	2045.2(13)
Z	4	4
T/K	293	293
ϱ_{calcd}/g cm^{-3}	1.836	1.751
λ/Å	0.710 73 (Mo)	0.710 73 (Mo)
μ/cm^{-1}	14.1	12.5
R^a	0.0491	0.0460
$R_w{}^b$	0.0566	0.0451

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$, $w^{-1} = \sigma^2(F) + 0.0006F^2$.

Preparation of [2·Ag]BF_4 (6). To a solution of **2** (100 mg; 0.33 mmol) in CH_3OH (30 mL) was added $AgBF_4$ (65 mg; 0.33 mmol). The reaction mixture was kept in the dark while being stirred at room temperature for 30 min. By evaporation of the methanol solution, the product was isolated in nearly quantitative yield as colorless crystals suitable for X-ray diffraction. The crystals were then washed with chloroform to afford pure **6**: ^1H NMR (CD_3OD) δ 3.50 (4 H, t, SCH_2), 3.63 (12 H, m, OCH_2); ^{13}C NMR (CD_3OD) δ 37.36, 68.31, 70.80, 70.88, 112.83, 123.09. Anal. Calcd for $C_{12}H_{16}N_2O_3S_2AgBF_4$: C, 29.15; H, 3.26; N, 5.67. Found: C, 28.83; H, 3.10; N, 5.61.

Preparation of [3·Ag]BF_4 (7). To a solution of **3** (100 mg; 0.29 mmol) in CH_3OH (30 mL) was added $AgBF_4$ (56.2 mg; 0.29 mmol). The reaction mixture was kept in the dark while being stirred at room temperature for 30 min. The solution was then concentrated to 20% of its original volume. The addition of diethyl ether produced the product as colorless crystals. X-ray-quality crystals were grown by vapor diffusion of ethyl ether into a methanol solution: ^1H NMR (CD_3OD) δ 3.47 (4 H, t, SCH_2), 3.60 (12 H, m, OCH_2), 3.67 (4 H, t, OCH_2); ^{13}C NMR (CD_3OD) δ 37.33, 68.18, 70.72, 71.44, 71.85, 112.79, 122.38. Anal. Calcd for $C_{14}H_{20}N_2O_4S_2AgBF_4$: C, 31.23; H, 3.75; N, 5.21. Found: C, 30.96; H, 3.54; N, 5.18.

Preparation of 3·$HgCl_2$ (8). We recently reported the X-ray structural determination of this complex.[10]

To a room-temperature solution of **3** (80 mg; 0.23 mmol) in CH_3OH (20 mL) was added $HgCl_2$ (65 mg; 0.23 mmol). The product formed immediately as a white precipitate and was then collected by filtration and washed with methanol and ethyl ether. X-ray-quality, colorless crystals were grown by ether diffusion into a chloroform solution of **8**: ^1H NMR ($CDCl_3$) δ 3.48 (4 H, t, SCH_2), 3.70 (12 H, m, OCH_2), 3.84 (4 H, t, OCH_2); ^{13}C NMR ($CDCl_3$) δ 36.18, 67.28, 69.67, 69.86, 70.47, 111.59, 121.57. Anal. Calcd for $C_{14}H_{20}N_2O_4S_2HgCl_2$: C, 27.27; H, 3.27; N, 4.55. Found: C, 27.28; H, 2.93; N, 4.38.

Single-Crystal X-ray Analysis. Single crystals of complexes **6** and **7** suitable for X-ray analysis were prepared as described above. Crystals were mounted on quartz fibers with epoxy resin. Accurate unit cell parameters for each compound were obtained by means of least-squares analysis of 20 centered reflections. Data for both compounds were collected on a Siemens P4/PC diffractometer using graphite-monochromated Mo Kα radiation. A summary of the crystallographic data and data collection and refinement parameters is given in Table 1. Two

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Complex **6**

Ag(1)	*x*	*y*	*z*	*U*(eq)[a]
Ag(1)	951(1)	5882(1)	2513(1)	57(1)
S(1)	3492(2)	5299(1)	3469(1)	61(1)
C(2)	2536(6)	4112(3)	2827(4)	48(2)
C(3)	1886(7)	3698(4)	1865(4)	47(2)
S(4)	1945(2)	4326(1)	1215(1)	65(1)
C(5)	37(10)	3758(5)	227(4)	71(3)
C(6)	−1619(9)	4016(5)	514(5)	72(3)
O(7)	−1584(7)	5005(3)	869(3)	80(3)
C(8)	−3131(11)	5363(7)	1090(7)	112(6)
C(9)	−3257(9)	5622(6)	2044(6)	88(4)
O(10)	−1835(6)	6325(4)	2682(3)	89(3)
C(11)	−2229(8)	6367(12)	3510(7)	202(26)
C(11*)	−1899(12)	6872(8)	3642(4)	75(6)
C(12)	−740(12)	6916(9)	4365(4)	170(24)
C(12*)	−1072(8)	6411(11)	4224(7)	107(13)
O(13)	697(7)	6429(4)	4243(3)	88(3)
C(14)	1169(9)	5789(4)	4613(4)	64(3)
C(15)	2993(8)	5683(4)	4623(4)	65(3)
C(16)	2585(7)	3586(4)	3343(4)	52(2)
N(17)	2648(8)	3215(4)	3801(4)	76(3)
C(18)	1221(7)	2718(4)	1345(4)	50(2)
N(19)	691(7)	1951(4)	896(4)	68(3)
B(1)	2822(6)	7689(3)	2533(4)	81(5)
F(11)	1619(10)	7544(7)	2913(7)	85(6)
F(12)	3294(16)	6883(7)	2006(8)	150(10)
F(13)	2219(19)	8087(10)	1996(10)	229(21)
F(14)	4157(13)	8247(10)	3222(7)	284(19)
F(1)	3802(15)	7412(10)	3102(9)	172(11)
F(2)	2989(25)	7251(12)	1651(6)	363(28)
F(3)	3044(14)	8608(5)	2882(13)	181(15)
F(4)	1194(8)	7330(8)	2291(13)	182(17)
Ag(1′)	−2952(1)	10439(1)	2209(1)	61(1)
S(1′)	−5970(2)	10940(1)	1573(1)	48(1)
C(2′)	−6997(6)	10919(3)	2424(3)	39(2)
C(3′)	−6135(7)	11201(3)	3328(4)	46(2)
S(4′)	−3947(2)	11639(1)	3755(1)	60(1)
C(5′)	−3294(11)	11308(5)	4701(5)	89(4)
C(6′)	−3041(9)	10306(5)	4340(5)	75(4)
O(7′)	−1792(7)	10163(4)	3823(4)	95(3)
C(8′)	−1207(15)	9269(8)	3518(8)	133(7)
C(9′)	−2155(14)	8587(6)	2690(8)	123(6)
O(10′)	−2439(9)	8802(4)	1920(4)	111(4)
C(11′)	−3602(13)	8043(4)	1140(7)	106(9)
C(11#)	−2654(21)	8228(11)	929(5)	83(6)
C(12′)	−4018(19)	8237(6)	298(4)	148(11)
C(12#)	−4494(24)	8152(3)	417(12)	137(15)
O(13′)	−4834(6)	9051(3)	533(4)	84(3)
C(14′)	−6619(9)	9007(5)	445(5)	79(3)
C(15′)	−7135(7)	9901(5)	495(4)	70(3)
C(16′)	−8827(7)	10709(4)	2162(4)	54(3)
N(17′)	−10272(6)	10548(4)	1972(4)	70(3)
C(18′)	−7059(9)	11210(4)	4011(4)	65(3)
N(19′)	−7700(10)	11221(5)	4573(5)	95(4)
B′	7170(10)	3309(5)	2529(5)	65(3)
F(11′)	8557(7)	3914(4)	2696(5)	138(4)
F(12′)	6436(11)	3577(8)	3201(5)	216(8)
F(13′)	5960(10)	3317(6)	1786(4)	176(5)
F(14′)	7603(12)	2463(5)	2247(10)	267(11)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotopic Displacement Coefficients ($Å^2 \times 10^3$) for Complex **7**

	x	*y*	*z*	*U*(eq)[a]
S(1)	4021(5)	2067(3)	4793(2)	95(2)
C(2)	3598(16)	2783(8)	3908(7)	68(5)
C(3)	4491(13)	3106(8)	3361(7)	53(4)
S(4)	6166(3)	2750(2)	3452(2)	63(1)
C(5)	6753(15)	2984(11)	2397(9)	91(6)
C(6)	8195(15)	2604(13)	2366(12)	103(7)
O(7)	8192(10)	1501(9)	2523(8)	99(5)
C(8)	9523(18)	1128(16)	2641(15)	117(9)
C(9)	9507(19)	135(21)	3057(16)	154(13)
O(10)	8920(11)	172(7)	3826(8)	103(4)
C(11)	8876(20)	−805(15)	4315(14)	135(9)
C(12)	8213(25)	−684(19)	5062(13)	143(11)
O(13)	6860(15)	−408(9)	4940(7)	110(5)
C(14)	5989(24)	−1263(16)	4969(13)	135(11)
C(15)	4638(23)	−865(16)	4996(12)	137(10)
O(16)	4298(11)	−285(8)	4268(6)	91(4)
C(17)	3045(17)	154(11)	4259(10)	91(7)
C(18)	2760(16)	1048(9)	4855(9)	91(6)
C(19)	2238(18)	3089(10)	3784(10)	79(6)
N(20)	1152(13)	3340(10)	3749(9)	103(5)
C(21)	4137(12)	3807(10)	2709(8)	56(4)
N(22)	3832(12)	4392(8)	2200(7)	75(4)
B	3299(20)	1107(13)	1621(12)	79(7)
F(1)	2486(14)	259(8)	1808(7)	151(5)
F(2)	2493(14)	1905(8)	1623(11)	211(9)
F(3)	3821(18)	895(16)	953(8)	267(11)
F(4)	4144(17)	1290(13)	2181(10)	240(9)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

standard reflections were monitored every 50 min, and these showed no significant variation over the data collections. The data were corrected for Lorentz and polarization factors, and for compound **6** a face-indexed numerical absorption correction was carried out. Both structures were solved by direct methods and refined by full-matrix least-squares procedures using anisotropic thermal parameters for the major occupancy non-hydrogen atoms. In complex **6** there is disorder in both crystallographically independent macrocyclic rings. In one molecule, two alternate site occupancies each of 50% were identified for C(11) and C(12); in the other, two alternate positions for C(11′) and C(12′) each of 65% and 35% occupancies. In both structures there was evidence of disorder in the BF_4 ions. In **6** this was resolved into two 50% occupancy orientations for one of the ions [(F(1)−F(4) and F(11)−F(14)] but not for the others. For compound **7**, which crystallizes in a noncentrosymmetric space group, the absolute structure was determined by the refinement of a free variable η which multiplies all F''; this variable refined to a value of 1.3(2), providing a definitive assignment. In both structures, hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. Computations were carried out on a 50-MHz 486 PC using the SHELXTL program system.[15] Fractional atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms in complexes **6** and **7** are given in Tables 2 and 3, respectively. Tables 4 and 5 give selected bond lengths and angles for **6** and **7**, respectively.

Results and Discussion

Ligand Synthesis. Ligands **2** and **3** were first prepared by Holdt and Teller in 11% and 12% yields, respectively, from disodium dithiomaleonitrile and dichloro derivatives of tetra- and pentaethylene glycol in protic media (ethanol/water).[14] A more recent report indicates an increase in the yields to 15−18% by a similar procedure.[6] In order to facilitate the study of these ligands, we sought a higher-yielding, general synthetic method. Several modifications to the existing procedure increased the yields in the critical crown-forming reactions to 48% and 35% for **2** and **3**, respectively (Scheme 1).

Specifically, we reacted disodium dithiomaleonitrile with the more reactive ditosylates of tetra- and pentaethylene glycol in a polar, aprotic medium, DMF. It has been shown that α,ω-ditosylates typically produce better yields in comparison to analogous dichloro systems for the synthesis of saturated polyazamacrocycles.[16] In addition, reactant concentrations of 15−17.5 mM were used, as compared to 36 mM in the method of Holdt and Teller,[14] to reduce the formation of polymeric byproducts.

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(15) Sheldrick, G. M. *SHELXTL PC*, Revision 4.2; Siemens Analytical X-Ray Instruments Inc.: Madison, WI, 1990.

(16) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268.

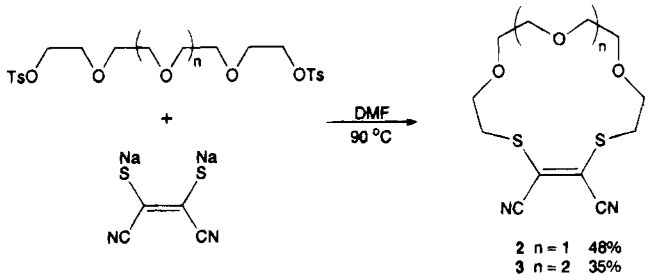
Table 4. Selected Bond Lengths (Å) and Angles (deg) for **6** with Estimated Standard Deviations in Parentheses

	Monomeric Form		
	Bond Lengths (Å)		
Ag(1)−S(1)	2.732(2)	Ag(1)−O(13)	2.579(6)
Ag(1)−O(10)	2.399(5)	Ag(1)−F(4)	2.510(18)
Ag(1)−F(11)	2.456(11)	Ag(1)−O(7)	2.705(6)
Ag(1)−S(4)	2.718(2)		
	Bond Angles (deg)		
S(1)−Ag(1)−S(4)	71.2(1)	S(1)−Ag(1)−O(13)	69.9(1)
S(4)−Ag(1)−O(10)	132.2(1)	O(10)−Ag(1)−O(13)	68.6(2)
S(4)−Ag(1)−O(13)	133.8(2)	S(4)−Ag(1)−F(11)	129.5(2)
S(1)−Ag(1)−F(11)	112.6(2)	O(13)−Ag(1)−F(11)	88.6(3)
O(10)−Ag(1)−F(11)	82.4(2)	S(4)−Ag(1)−F(4)	116.1(4)
S(1)−Ag(1)−F(4)	126.9(2)	O(13)−Ag(1)−F(4)	106.9(4)
O(10)−Ag(1)−F(4)	81.3(3)	Ag(1)−S(1)−C(15)	102.8(2)
Ag(1)−S(1)−C(2)	93.5(2)	Ag(1)−S(4)−C(3)	94.0(2)
Ag(1)−S(4)−C(5)	104.7(2)	Ag(1)−O(10)−C(9)	115.4(4)
Ag(1)−O(10)−C(11)	113.6(5)	Ag(1)−O(13)−C(12*)	107.7(5)
Ag(1)−O(13)−C(12)	108.4(5)	Ag(1)−F(11)−B(1)	113.0(6)
Ag(1)−O(13)−C(14)	114.4(4)	Ag(1)−F(11)−B(1)	113.0(6)
Ag(1)−F(4)−B(1)	110.0(9)	S(1)−Ag(1)−O(10)	135.3(2)
O(10)−Ag(1)−O(7)	66.0(2)	O(7)−Ag(1)−S(4)	69.5(2)
	Polymeric Form		
	Bond Lengths (Å)		
Ag(1′)−S(1′)	2.711(2)	Ag(1′)−O(13′)	2.682(7)
Ag(1′)−O(10′)	2.516(7)	Ag(1′)−O(7′)	2.802(6)
Ag(1′)−S(4′)	2.683(2)	N(17′)−Ag(1A)	2.276(6)
Ag(1′)−N(17A)	2.276(6)		
	Bond Angles (deg)		
S(1′)−Ag(1′)−O(10′)	126.1(1)	Ag(1′)−S(1″)−C(15′)	106.1(2)
S(1′)−Ag(1′)−S(4′)	72.5(1)	Ag(1′)−S(4′)−C(3′)	97.5(2)
S(1′)−Ag(1′)−N(17A)	133.2(2)	Ag(1′)−S(4′)−C(5′)	108.9(3)
S(4′)−Ag(1′)−N(17A)	125.3(1)	Ag(1′)−O(10′)−C(9′)	119.6(5)
S(4′)−Ag(1′)−O(10′)	122.2(2)	Ag(1′)−O(10′)−C(11′)	117.2(5)
O(10′)−Ag(1′)−N(17A)	83.9(2)	Ag(1′)−O(10′)−C(11,	108.7(8)
S(4′)−Ag(1′)−O(7′)	66.2(2)	O(7′)−Ag(1′)−O(10′)	62.6(2)
O(10′)−Ag(1′)−O(13′)	65.2(2)	O(13′)−Ag(1′)−S(1′)	67.9(2)
Ag(1′)−S(1′)−C(2′)	97.2(2)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **7** with Estimated Standard Deviations in Parentheses

	Bond Lengths (Å)		
Ag−S(4)	2.533(3)	Ag···S(1)	3.315(3)
Ag−O(13)	2.501(11)	Ag−O(10)	2.714(11)
Ag−O(16)	2.593(11)	Ag···O(7)	2.859(11)
Ag−N(22A)	2.310(10)		
	Bond Angles (deg)		
S(4)−Ag−O(13)	137.6(3)	S(4)−Ag−O(16)	120.7(2)
O(13)−Ag−O(16)	66.8(4)	S(4)−Ag−N(22A)	127.9(3)
O(13)−Ag−N(22A)	94.4(4)	O(16)−Ag−N(22A)	76.8(4)
Ag−S(4)−C(5)	107.8(5)	Ag−S(4)−C(3)	109.3(4)
Ag−O(13)−C(12)	117.1(11)	Ag−O(13)−C(14)	110.7(11)
Ag−O(16)−C(17)	121.1(8)	Ag−O(16)−C(15)	110.2(11)
S(4)−Ag−O(10)	110.4(3)	O(10)−Ag−O(13)	65.9(4)
C(21)−N(22)−Ag(A)	166.6(11)		

Scheme 1



Metal Complex Formation. Silver(I) complexes were prepared by reacting 1 equiv of $AgBF_4$ with 1 equiv of either ligand **2** or **3** in methanol at room temperature. Complexation is rapid and proceeds in nearly quantitative yields. Both complexes are air stable and, as crystalline solids, show no appreciable sensitivity to light.

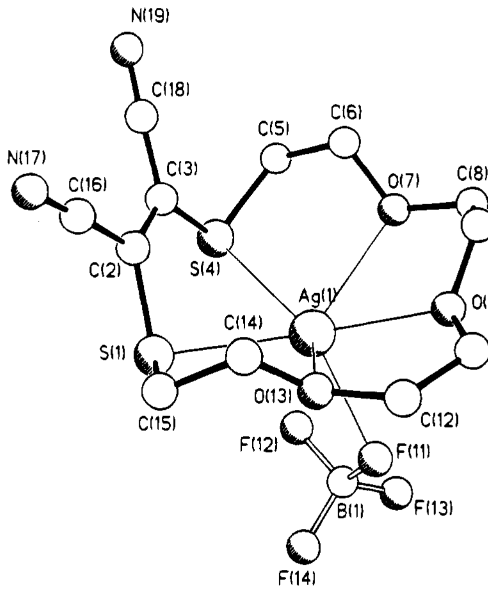


Figure 1. View of the monomeric form of complex **6** showing the atom-numbering scheme adopted.

Table 6. Selected ^{13}C NMR and IR Data for Compounds **2**, **3**, and **6**−**8**

	2	3	6	7	8
		δ (ppm), CH_2O(avg)			
CD_3OD	71.43	71.73	70.00	70.55	
$CDCl_3$	69.96	70.49			69.32
		δ (ppm), CH_2S			
CD_3OD	35.97	35.88	37.36	37.33	
$CDCl_3$	34.83	34.92			36.18
		ν_{CN} (cm^{-1})[a]			
KBr disk	2212	2209	2226	2210, 2251	2210

[a] KBr disk.

The most striking feature in the IR spectra of **6** and **7** in the solid state is the increase in the nitrile stretching frequency relative to that of the uncomplexed macrocycles **2** and **3** (see Table 6). For **6**, the CN stretch occurs at 2226 cm^{-1} as compared to 2212 cm^{-1} for the free ligand **2**. For **7**, two distinct CN stretches are observed, 2251 and 2210 cm^{-1}, as compared to 2209 cm^{-1} for free ligand **3**, indicating the presence of two distinct nitrile moieties. Purcell and Drago showed that interaction of the nitrile unit with a Lewis acid increases its stretching frequency by increasing the CN force constant.[17] The observed CN frequencies of **6** and **7** are then evidence for the *coordination* of the nitrile to the Ag(I) ion. Further, for complex **7**, the resolution of two CN bands indicates the presence of both complexed and "free" nitrile moieties. In contrast, there is no change in the CN stretching frequency upon complexation of $HgCl_2$ (complex **8**). In this case coordination to the Hg atom does not involve either nitrile functionality and is through the macrocyclic O atoms alone.[10]

X-ray Structure of [2·Ag]BF₄ (6). Complex **6** crystallizes with two molecules per asymmetric unit. Both are 1:1 Ag(I)-to-ligand species with one as a monomer and the other as part of a polymer chain. As shown in Figure 1, the monomeric form consists of a Ag(I) ion in a distorted pentagonal pyramid coordinated by all five macrocyclic donor atoms in an *endo* manner and a fluorine atom from the BF_4 anion. Atoms S(1), S(4), O(7), O(10), and O(13) are coplanar to within 0.12 Å,

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[17] Purcell, K. F.; Drago, R. S. *J. Am. Chem. Soc.* **1966**, *88*, 919.

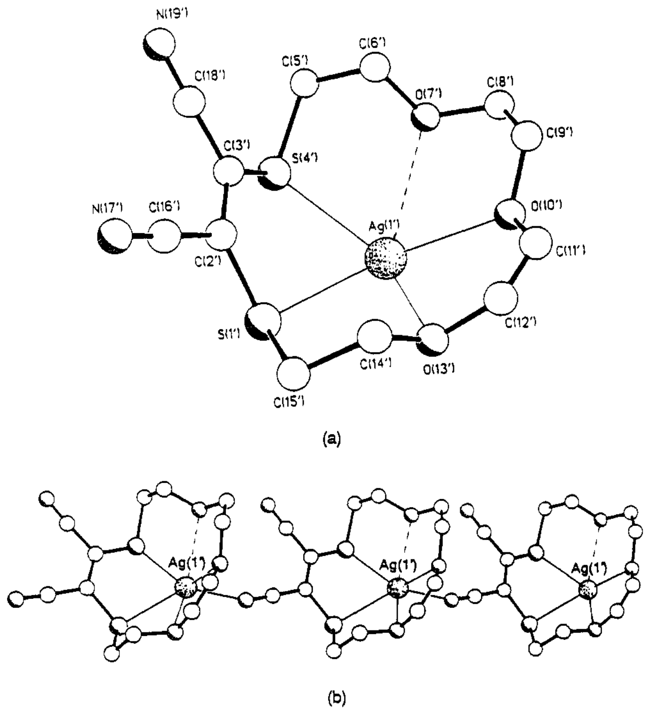

Figure 2. (a) View of the macrocyclic unit in the polymeric form of complex **6** showing the atom-numbering scheme adopted. (b) View of the linear-chain polymer formed by complex **6**. The BF_4^- anions have been omitted for clarity.

and the Ag atom lies 0.70 Å out of this plane in the direction of the coordinated F atom. The bond lengths for Ag–S (Ag(1)–S(1) = 2.732(2) Å; Ag(1)–S(4) = 2.718(2) Å) and Ag–O (Ag(1)–O(7) = 2.750(6) Å; Ag(1)–O(10) = 2.399(5) Å; Ag(1)–O(13) = 2.579(6) Å) compare reasonably well with corresponding literature values, the Ag–O(7) bond being somewhat long.[18,19] The Ag(1)–F(11) bond length is 2.456(11) Å. The bond angles of the five-membered chelate rings all fall in the range 66–72° (see Table 4).

The structure of the polymeric form of **6** is depicted in Figure 2. As in the monomer, the Ag(I) ion is coordinated by an approximately pentagonal pyramidal ligand environment. Again, all five macrocyclic donor atoms interact in an *endo* manner, with the sixth ligand being a nitrile moiety from an adjacent [**2**·Ag] unit. Atoms S(1′), S(4′), O(7′), O(10′), and O(13′) are coplanar to within 0.04 Å with the Ag atom lying 0.93 Å out of this plane in the direction of the coordinated cyano N atom (N(17′)). The intrachain Ag···Ag distance is 8.02 Å. The bond lengths for Ag–S (Ag(1′)–S(1′) = 2.711(2) Å; Ag(1′)–S(4′) = 2.683(2) Å) and Ag–O (Ag(1′)–O(7′) = 2.802(6) Å; Ag(1′)–O(10′) = 2.516(7) Å; Ag(1′)–O(13′) = 2.682(7) Å) are similar to those of the monomer. The Ag(1′)–O(7′) bond is longer than what is typically observed for a Ag–O bond,[19] indicating a largely electrostatic interaction. A slight lengthening of all three Ag–O bonds in the polymer may be due to a stronger interaction of the $N_{nitrile}$ donor atom vs the F atom of the coordinated BF_4 anion in the monomer form. The Ag–N bond (Ag(1′)–N(17A) = 2.276(6) Å) is the shortest of all the coordinate bonds in **6**; it is equal in length to that reported for coordinated CH_3CN ligands (2.27(1) Å).[18a] The bond angles of the five-membered chelate rings are all in the range 62–73° (Table IV).

The local environments about the Ag(I) ion in the two different forms of **6** are very similar. In both cases, ligand **2** interacts with the Ag(I) ion through the endocyclic coordination of all five of its heteroatoms. The two molecules differ in the remaining ligand. In the polymer the nitrile moiety of one molecule coordinates to the Ag(I) ion of an adjacent molecule. Such a polymer can be disrupted by replacement of the nitrile ligand with another suitable donor, and in the structure of the monomeric form of **6** a fluorine atom from the BF_4 anion can be viewed as serving this purpose.

Blake et al. recently reported polymeric Ag(I) complexes of the related macrocycles **4**[3a] and 1,4,7,10,13-pentathiacyclopentadecane ([15]aneS_5).[18e] In these complexes the crown encircles the Ag(I) ion in an *endo* manner, as in **6**. However, the mechanism for linking the individual molecules to form a polymer is quite different. In both of the complexes reported by Blake et al. one of the macrocyclic S atoms bridges to another AgL (L = [15]aneS_2O_3 or [15]aneS_5) unit to form the linear-chain polymer. In **6**, however, linking occurs by coordination of a $N_{nitrile}$ donor atom. An interesting structural similarity in the Ag(I) complexes of the saturated crown **4** and of ligand **2** (in both monomeric and polymeric forms) is that in both cases the shortest Ag–O bond (Ag(1)–O(10) in Figure 1 and Ag(1′)–O(10′) in Figure 2) is across the macrocycle from the two S atoms; this bond is roughly of the same length in the two complexes.

X-ray Structure of [3·Ag]BF$_4$ (7). In light of the polymeric structure of **6**, we anticipated the larger crown **3** stabilizing a Ag(I) center through the coordination of all six macrocyclic heteroatoms, resulting in discrete monomeric complexes. As shown in Figure 3, however, the structure consists of a linear-chain polymer of endocyclic, 1:1 metal-to-ligand molecular units (interchain Ag···Ag distance = 7.92 Å) with the links between the [**3**·Ag] units again provided by a Ag–$N_{nitrile}$ bond.

The Ag(I) ion in **7** is best described as being at the center of a distorted square pyramidal array of one S, three O, and one N donor atoms. Three of the four macrocyclic O atoms are coordinated (Ag–O(10) = 2.714(11) Å; Ag–O(13) = 2.501(11) Å; Ag–O(16) = 2.593(11) Å) along with only one of the two available S atoms (Ag–S(4) = 2.533(3) Å). The remaining O atom, O(7), interacts with the Ag(I) ion (Ag–O(7) = 2.859(11) Å), but at a distance beyond what is normally observed for Ag–O_{ether} bonds.[19] Surprisingly, the uncoordinated S atom, S(1), is 3.315(3) Å from the Ag(I) center, considerably longer than typical Ag–S bonds.[18] The fifth ligand, a N atom from the nitrile moiety of an adjacent [**3**·Ag] unit, is at a distance (Ag–N(22A) = 2.310(10) Å) similar to that in complex **6**. The structure thus confirms that the two CN stretches present in the IR spectrum of **7** are a result of Ag(I) coordination to one of the two nitriles of each malonitrile unit. The four S(4)–Ag–L (L = O(10), O(13), O(16), N(22A)) bond angles are S(4)–Ag–O(10) = 110.4(3)°, S(4)–Ag–O(13) = 137.6(3)°, S(4)–Ag–O(16) = 120.7(2)°, and S(4)–Ag–N(22A) = 127.9(3)°, whereas those for the L–Ag–L angles are O(10)–Ag–O(13)

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(18) For examples of structurally characterized Ag(I) complexes with thioether crowns see: (a) de Groot, B.; Loeb, S. J.; Shimizu, G. K. H. *Inorg. Chem.* **1994**, *33*, 2663. (b) Loeb, S. J.; Shimizu, G. K. H. *Inorg. Chem.* **1993**, *32*, 1001. (c) de Groot, B.; Jenkins, H. A.; Loeb, S. J. *Inorg. Chem.* **1992**, *31*, 203. (d) de Groot, B.; Loeb, S. J. *Inorg. Chem.* **1991**, *30*, 3103. (e) Blake, A. J.; Collison, D.; Gould, R. O.; Reid, G.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1993**, 521. (f) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Schröder, M. *Polyhedron* **1989**, *8*, 513. (g) Blower, P. J.; Clarkson, J. A.; Rawle, S. C.; Hartmen, J. R.; Wolf, R. E., Jr.; Yagbasan, R.; Bott, S. G.; Cooper, S. R. *Inorg. Chem.* **1989**, *28*, 4040.

(19) For examples of structurally characterized Ag(I) complexes with crown ethers see: (a) Bradshaw, J. S.; McDaniel, C. W.; Skidmore, B. D.; Nielsen, R. B.; Wilson, B. E.; Dalley, N. K.; Izatt, R. M. *J. Heterocycl. Chem.* **1987**, *24*, 1085. (b) Jones, P. G.; Gries, T.; Grützmacher, H.; Roesky, H. W.; Schimkowiak, J.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 376. (c) Roesky, H. W.; Peymann, E.; Schimkowiak, J.; Noltemeyer, M.; Pinkert, W.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1983**, 981.

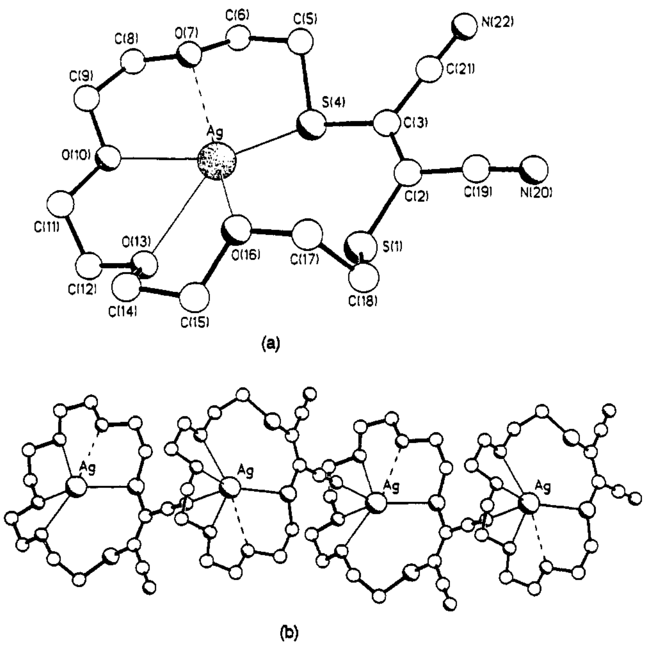

Figure 3. (a) View of the macrocyclic unit in the polymeric complex **7** showing the atom-numbering scheme adopted. (b) View of the linear-chain polymer formed by complex **7**. The BF_4^- anions have been omitted for clarity.

= 65.9(4)°, O(13)−Ag−O(16) = 66.8(4)°, and O(16)−Ag−N(22A) = 76.8(4)° (see Table 5). This suggests viewing the Ag(I) ion as having a distorted square pyramidal coordination with S(4) at the apex. However, the variation in bond lengths and angles seen in **7** is not uncommon in Ag(I) macrocyclic complexes.[18,20] Thus, the two relatively long Ag−O interactions (Ag−O(7), Ag−O(10)) in **7**, coupled with the weak stereochemical preferences of Ag(I),[18g] do not rule out a description of the Ag(I) ion as four- (distorted tetrahedral array of N(22A), S(4), O(13), O(16)) or six-coordinate (distorted octahedral array of (N(22A), S(4), O(7), O(10), O(13), O(16)).

The coordination of only one S donor atom to the thiophilic Ag(I) ion was unexpected because it was thought that both S atoms would be needed to stabilize a 1:1 complex involving O_{ether} donors, as seen in **4**·Ag[3a] and **6**. Instead, as in the $HgCl_2$ complex **8**, coordination is primarily by the O donor atoms.

NMR Spectroscopic Studies. To examine the Ag coordination in solution, CD_3OD and CD_3CN solutions of **6** and **7** were studied by ^{13}C NMR spectroscopy. In CD_3OD the average structures of **6** and **7** retain C_2 symmetry as determined by the number of peaks present in their spectra. In addition, all of the macrocyclic methylene carbon resonances for **6** and **7** are shifted relative to those in the spectra of the free ligands (**2** and **3**, respectively). Therefore, in methanolic solutions, the integrity of each complex is maintained with all of the macrocyclic heteroatoms (both S and O) symmetrically coordinated to the Ag(I) ion. The ^{13}C methylene resonances next to the O atoms shift upfield upon complexation (see Table 6). Similar upfield shifts are observed for the complexation of alkali metals by crown ethers and are ascribed to a change in the conformation of the polyether moiety upon metal binding.[21] The methylene resonances next to the S atom, however, shift downfield in both **6** and **7**. Methylene resoances next to S atoms are relatively insensitive to conformational changes.[22] Shifts upon complexation, presumably a result of polarization of the C−S bond, then, are expected to be downfield. Similar shifts in the macrocyclic methylene resonances were previously reported for the $HgCl_2$ complex **8** in $CDCl_3$ (Table 6).[10]

We note, however, in CD_3CN the ^{13}C NMR spectrum of **6** is identical to the spectrum of uncomplexed ligand **2**. This indicates that acetonitrile effectively scavenges the Ag(I) ion from the oxathioether crown.

Conclusion

We have prepared ligands **2** and **3** by an improved procedure and structurally characterized their endocyclic Ag(I) complexes, **6** and **7**. A comparison to **3**·$HgCl_2$, **8**, whose properties were reported recently,[10] reveals the following. (1) In the solid state the metal ion of each of the three complexes is bound in an *endo* manner, but asymmetrically, by the macrocyclic ligand. In each case nearly all of the O donor atoms interact to some extent with the metal center. However, the contributions of the S atoms to the stabilities of the complexes are different in the three structures. In **8**, coordination is primarily through two O atoms without bonding to the two S atoms; in **7**, one S atom is coordinated to the metal; in **6**, both S atoms are coordinated. (2) ^{13}C NMR studies confirm that the metal ions in **6** and **7** (in methanol) and **8** (in chloroform) remain coordinated in solution and that the average structures are symmetrical. Thus, it is possible that the structures in solution exhibit the full denticity of the respective macrocycles. Alternatively, the instantaneous structure could be unsymmetrical, as in the solid, with fluxional processes producing an averaged NMR spectrum.

Though the effects remain to be quantified, the contribution of the S atoms to complex stability appears to be weaker in **6**, **7** and **8** than in analogous complexes with saturated oxathioether crowns (e.g. **4** and **5**). Hence, while the coordination of the metal ion varies markedly in the two Ag(I) complexes of **4**[3a] and the $HgCl_2$ complexes of **5**[5b] and 1,4,13,16-tetraoxa-7,10-dithia[16](1,1′)ruthenocenophane,[5a] all of these complexes involve chelation of both available macrocyclic S atoms, in contrast to the results here. It appears then that the electron-withdrawing maleonitrile unit weakens the donating ability of the macrocyclic S atoms. Nonetheless, stable heavy metal adducts are readily formed.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 9408561).

Supplementary Material Available: Tables of calculated atomic coordinates and isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters, and complete bond distances and angles for **6** and **7** (7 pages). Ordering information is given on any current masthead page.

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