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Synthesis and X-Ray Crystal Structure of New Oxathiacrown Ethers Containing Sulfoxide Group and Their Metal-Binding Properties: Highly Selective Receptors for Ag^+ and Cu^{2+}*

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Abstract

Three new oxathiacrown ethers **1**, **2** and **3** containing a sulfoxide group were synthesized in a simple way. Conductometric titration studies in pure acetonitrile were employed to invistigate their binding affinities towards Ag^+, Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+} and Hg^{2+}. They were found to be selective for Ag^+ and Cu^{2+} over the other metals investigated. Ligand **1** has the highest selectivity towards Ag^+. The structure of compound **3** was confirmed by X-ray crystallography.

Introduction

Highly selective reagents for metal ions are of great interest area for analytical and separation chemistry [1–5]. An important parameter in the study of macrocyclic ligand–metal complexes is the stability constant K_{assoc}. The magnitudes of these stability constants are governed by several factors including the relative size of the cation and the macrocyclic cavity (ring size effect), the number and the nature of binding sites, the acid–base character of metal ions and the nature of the solvent [6]. All of these factors also affect the selectivity of the macrocyclic ligands towards cation. Such compounds that have been studied extensively during the past four decades are crown ethers since they were first prepared and recognized to have selective metal-ion binding properties by Pedersen [7]. Crown ethers that contain hard donor atoms such as oxygen atoms mainly complex alkali or alkaline earth metal ions, whereas those containing soft donor atoms such as nitrogen or/and sulfur atoms bind heavy metal ions [8–16]. Also, it has been shown that phosphine oxide (P=O) and/or sulfoxide (S=O) groups are good ligating sites for alkali, alkaline earth, transition, actinide metal ions and monoalkylammonium ions when they are incorporated into the macrocycle [17–20].

To the best our knowledge, general procedure for preparing thiacrown ethers containing sulfoxide groups has not been reported yet. In this manuscript we report the synthesis of new oxathiacrown ethers containing sulfoxide group and preliminary investigation of their metal cation-binding properties evaluated by conductance titration technique. Our studies have focused on the complexation behaviour of the industrially important ions: Ag^+, Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+} and Hg^{2+} for the purpose of developing new reagents for the sensing and separation of metal ions.

Experimental

Melting points are uncorrected. ^{1}H NMR spectra were recorded on a 200 MHz spectrometer. In all cases, samples were dissolved in $CDCl_3$ using TMS as internal standard. All reagents were of analytical grade and used without further purification. Chromatographic separations were carried out on thin layer chromatography (TLC) using silica gel GF254 (Fluka). Unless otherwise noted, all reactions were carried out under dry nitrogen. Compounds **4**, **5** and **6** were prepared according to literature procedures [21]. The following salts were obtained from the suppliers indicated: $AgNO_3$ (GCC, 99%), $Cu(ClO_4)_2 \cdot 6H_2O$ (Aldrich), $Zn(ClO_4)_2 \cdot 6H_2O$ (Aldrich), $Cd(ClO_4)_2$ (Aldrich), $MnCl_2 \cdot 4H_2O$ (Aldrich), $Cr(NO_3)_3 \cdot 9H_2O$ (Aldrich), $Co(ClO_4)_2 \cdot 6H_2O$ (Alfa), $Ni(NO_3)_2 \cdot 6H_2O$ (BDH, 99%) and $HgBr_2$ (BDH, 98%). For conductivity experiments, acetonitrile (HPLC grade, GCC, assay 99.8%) was dried over calcium hydride and then double-distilled fractionally to give anhydrous solvent ($< 3 \times 10^{-7}$ S cm^{-1}). The description of the conductometer and the details of the conductance measurements have been given previously [22].

* **Supplementary Data** relevant to this article have been deposited at the Cambridge Crystallographic Data Centre under the deposition number 232076.

Synthesis

*Base mediated coupling of **6** with 2-mercaptoethyl ether to give 1,13-di-[(ethoxycarbonyl)methoxy]1,2,12,13-dibenzo-**7**-oxa-4,10-dithiatrideca-1,12-diene* (*7*). To 2-mercaptoethyl ether (0.51 g, 3.66 mmol) in 95% ethanol (50 ml) at room temperature was added KOH (0.45 g, 7.32 mmol). The reaction was left to stir for 1 h. A solution of **6** (1.67 g, 7.32 mmol) in benzene (20 ml) was added dropwise. The reaction was stirred for an additional 1h and then the mixture was filtered. The filtrate was extracted with $CHCl_3$ (50 ml). The organic layer was washed with water and dried over anhydrous $MgSO_4$ and evaporated to give **7** as colorless oil (1.61 g, 81%). The sample was pure enough for use in the subsequent step. An analytical sample was purified by TLC using ethyl acetate:hexane (3:8) eluent; ^{1}H NMR δ_H 1.29 (t, $J = 4$ Hz, 6H), 2.68 (t, $J = 5$ Hz, 4H), 3.60 (t, $J = 5$ Hz, 4H), 3.86 (s, 4H), 4.25 (q, $J = 4$ Hz, 4H), 4.66 (s, 4H), 6.75 (d, $J = 10$ Hz, 2H), 6.98 (t, $J = 8$ Hz, 2H), 7.14–7.32 (m, 4H); ^{13}C NMR δ_C 30.0, 30.8, 31.0, 61.8, 66.0, 70.9, 112.0, 122.0, 128.0, 128.5, 131.0, 155.8, 159.0; +APCI HRMS calcd for $C_{26}H_{34}S_2O_7$ $(M+1)^+$ 523.658, found 523.45 (100%).

LAH reduction of **7** *to give 1,19-dihydroxy-4,5,15,16-dibenzo-3,10,17-trioxa-7,13-dithianonadeca-4,15-diene* (**8**). To a suspension of LAH (0.45 g, 11.72 mmol) in anhydrous THF (50 ml) a solution of **7** (1.53 g, 2.93 mmol) in anhydrous THF (25 ml) at room temperature was added. The reaction mixture was stirred for 10 min and then poured into wet diethyl ether (100 ml) at 0 °C. The mixture was acidified with aqueous 10% HCl. The mixture was extracted with diethyl ether (30 ml). The organic layer was dried over anhydrous $MgSO_4$ and evaporated to give **8** as a colorless oil (1.06 g, 83%); ^{1}H NMR δ_H 2.64 (t, $J = 6$ Hz, 4H), 3.45 (br, 2H), 3.55 (t, $J = 6$ Hz, 4H), 3.81 (s, 4H), 3.93 (m, 4H), 4.15 (m, 4H), 6.81–6.95 (m, 4H), 7.20–7.29 (m, 4H); ^{13}C NMR δ_C 31.0, 31.8, 61.2, 70.0, 70.8, 112.2, 121.0, 127.0, 128.8, 131.0, 136.5; +APCI HRMS calcd for $C_{22}H_{30}S_2O_5$ $(M+1)^+$ 439.587, found 439.30 (100%).

General procedure for the synthesis of the oxathiacrown ethers **1**, **2** *and* **3**. To a solution of diols **4**, **5** or **8** (0.48 mmol) in dry dichloromethane (20 ml) at room temperature was added freshly distilled thionyl chloride (0.11 ml, 1.44 mmol). The reaction mixture was stirred at room temperature for 15–30 min and then was quenched by adding 20 ml of cold water. The organic layer was washed with water until the aqueous layer was neutral. After separation, the organic layer was dried over anhydrous $MgSO_4$ and evaporated to give crude product. The crude product was purified by TLC using ethyl acetate-hexane (3:7) eluent to give:

2,3,10,11-Dibenzo-1,12,15,17-tetraoxa-5,8,16-trithiacyclononadecane-2,10-diene-16-oxide (***1***). A colorless solid, yield 45%; mp 65–66 °C, ^{1}H NMR δ_H 2.70 (m, 4H), 3.75 (d, $J = 8$ Hz, 2H), 3.89 (d, $J = 8$ Hz, 2H), 4.22 (t, 4H), 4.48 (br, 4H), 6.84 (d, $J = 8$ Hz, 2H), 7.0 (t, $J = 8$ Hz, 2H), 7.20 (t, $J = 8$ Hz, 2H), 7.34 (d, $J = 8$ Hz, 2H); ^{13}C NMR δ_C 29.8, 31.5, 61.2, 67.0, 111.6, 122.0, 127.5, 128.6, 131.0, 156.0; +APCI HRMS calcd for $C_{20}H_{24}S_3O_5$ $(M+1)^+$ 441.586, found 441.25 (100%). Anal. Calcd for $C_{20}H_{24}S_3O_5$: C, 54.52; H, 5.49; S, 21.83, found: C, 54.68; H, 5.60; S, 21.59.

2,3,13,14-Dibenzo-1,15,18,20-tetraoxa-5,8,11,19-tetrathiacyclodocosane-2,13-diene-19-oxide (***2***). A colorless solid, yield 38%; mp 88.5–90 °C, ^{1}H NMR δ_H 2.59-2.90 (m, 8H), 3.78 (d, $J = 8$ Hz, 2H), 3.90 (d, $J = 8$ Hz, 2H), 4.19–4.28 (m, 4H), 4.30–4.60 (m, 4H), 6.82 (d, $J = 8$ Hz, 2H), 6.96 (t, $J = 8$ Hz, 2H), 7.20 (t, $J = 8$ Hz, 2H), 7.34 (d, $J = 8$ Hz, 2H); ^{13}C NMR δ_C 29.6, 31.9, 32.2, 61.0, 67.0, 111.8,121.9, 127.1, 128.1, 131.0, 156.1; +APCI HRMS calcd for $C_{22}H_{28}S_4O_5$ $(M+1)^+$ 501.703, found 501.40 (100%). Anal. Calcd for $C_{22}H_{28}S_4O_5$: C, 54.77; H, 6.64; S, 25.62, found: C, 54.68; H, 6.61; S, 25.55.

2,3,13,14-Dibenzo-1,8,15,18,20-pentaoxa-5,11,19-trithiacyclodocosane-2,13-diene-19-oxide (**3**). A colorless solid, yield 30%; mp 79.0–80.5 °C, ^{1}H NMR δ_H 2.66 (t, $J = 8$ Hz, 4H), 3.66 (t, $J = 8$ Hz, 4H), 3.78 (d, $J = 8$ Hz, 2H), 3.90 (d, $J = 8$ Hz, 2H), 4.20–4.25 (m, 4H), 4.30–4.58 (m, 4H), 6.82 (d, $J = 8$ Hz, 2H), 6.99 (t, $J = 6$ Hz, 2H), 7.20 (t, $J = 6$ Hz, 2H), 7.33 (d, $J = 8$ Hz, 2H); ^{13}C NMR δ_C 30.0, 31.0, 61.1, 66.8, 70.8, 111.8, 121.8, 127.5, 128.5, 131.0, 156.0, +APCI HRMS calcd for $C_{22}H_{28}S_3O_6$ $(M+1)^+$ 485.64, found 485.20 (100%). Anal. Calcd for $C_{22}H_{28}S_3O_6$: C, 54.52; H, 5.82; S, 19.85, found: C, 54.72; H, 5.89; S, 19.70.

X-ray crystallography and crystal structure of macrocycle ***3***

All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$). Crystal data and structure refinement for the ligand is shown in Table 1. Selected bond lengths, bond angles and torsional angles are given in Table 2. Colorless crystals of **3** suitable for X-ray analyses was obtained by slow evaporation of ethyl acetate/hexane (v/v 1:1) solution at room temperature. According to the X-ray structure (Figure 1), two aromatic planes are slightly twisted. In thia-crown ethers there is often a pronounced tendency to place the sulfur atoms *exodentate* to the macrocyclic cavity [23]. In the 22-membered ring of macrocycle **3** the three sulfur atoms S(1), S(2) and S(3) tend to be as far apart as possible from each other and away from the macrocyclic cavity. Therefore, the arrangement of sulfur atoms is best described as an *exodentate* with respect to the cavity. This is evident from the torsional angle values of C(7)—S(1)—C(8)—C(9), C(12)—S(2)—C(11)—C(10) and O(6)—S(3)—O(4)—C(20) that equal 72.1(3), 81.1(3) and 87.0(7), respectively. Also, it is clear that the S(1)—C(8)—C(9)—O(2) and O(2)—C(10)—C(11)—S(2) units disfavor the *gauche* conformations and arranged as *anti* and *exodentate*. On the other hand, the five oxygen atoms are arranged in two different ways. The oxygen

Table 1. Crystal data and structure refinement for macrocycle **3**

Formula	$C_{22}H_{28}O_6S_3$
M	484.64
T, K	299
Crystal system	Orthorhombic
Space group	Pbca (#61)
a/Å	38.800(4)
b/Å	13.650(8)
c/Å	8.856(4)
V/Å^3	4690(3)
Z	8
D_{calc}/gcm^{-3}	1.373
μ/cm^{-1}	3.51
F(000)	2048.00
Crystal size/mm	0.20 × 0.40 × 0.40
Number of reflections used for unit cell determination (2θ)	23 (8.6–28.0)
Omega scan peak width at half-height	0.22°
Radiation	MoKα (λ = 0.71069 Å)
Take-off angle	6.0
Scan type	ω-2θ
Scan rate	4.0°/min(in ω)(up to 5 scans)
Scan width	(1.01 + 0.35 tan θ)°
$2\theta_{max}$	55.1°
Number of reflections measured	6103
p-factor	0.0200
Number of observations [$I < 2.00\sigma(I)$]	2690
Number of variables	299
Reflections/parameter ratio	9.00
Residuals: *R*; R_w	0.055 ; 0.051
Goodness of fit indicator	1.62
Max. shift/error in final cycle	0.00
Max. peak in final diff. Map	0.46 e$^-$/ Å^3
Min. peak in final diff. Map	−0.28 e$^-$/ Å^3

atoms O(1), O(3), O(4) and O(6) are arranged inside the cavity as an *endo*-fashion orientation, whereas O(2) is out of the cavity. In contrast to the sulfur case, the O—C—C—O units are arranged as *gaushe* conformations. It is known that 1,4-interactions between heteroatoms (E = O, N or S) in the —E—CH_2CH_2—E— bond

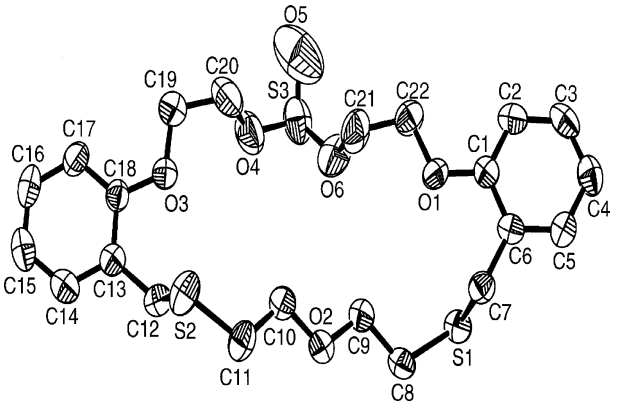


Figure 1. ORTEP plot of macrocycle **3**.

depend on whether E is a first-or second-row element [23]. For example, N and O heteroatoms stabilize the *gauche* conformation because of the dispersion forces between the hetero E atoms. In contrast, for E = S, the larger size of the atoms causes greater repulsion between electrons, which disfavors *gauche* conformations. The present rules readily apply to the structure of macrocycle **3** shown in Figure 1.

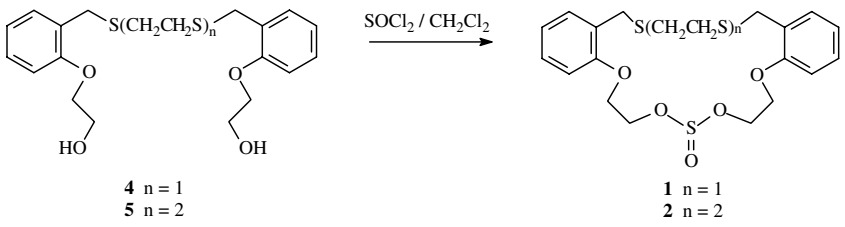
Results and discussion

Synthesis

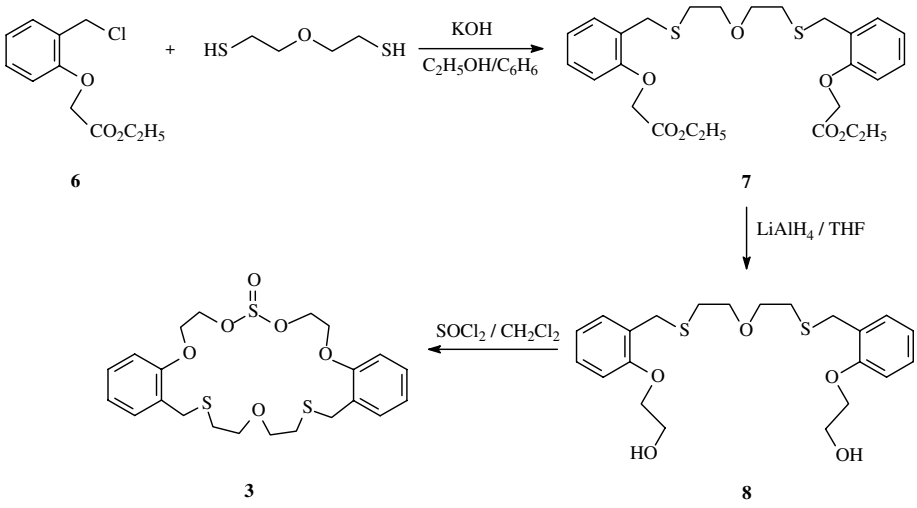
The synthesis of oxathiacrown ethers **1**, **2** and **3** were carried out as shown in Schemes 1 and 2. Compounds **4**, **5** and **6** were prepared previously [21]. Base-mediated coupling of compound **6** with 2-mercaptoethyl ether afforded 7 in 85% yield. LAH reduction of **7** in THF at room temperature produced **8** in 83% yield. Treatment of compounds **4**, **5** or **8** with freshly distilled thionyl chloride in anhydrous dichloromethane at room temperature for 0.5 h produced oxathiacrown ethers **1**, **2** and **3** as colorless solids in 45%, 38% and 30% yield, respectively, after thin layer chromatographic separation. The

Table 2. Selected bond lengths (Å), bond angles (°) and torsional angles (°) for macrocycle **3**

S(1)—C(7)	1.821(4)	S(1)—C(8)	1.809(4)
S(3)—O(4)	1.585(9)	S(3)—O(6)	1.60(1)
S(2)—C(12)	1.810(4)	S(2)—C(11)	1.797(4)
C(1)—O(1)	1.373(4)	C(22)—O(1)	1.412(4)
C(18)—O(3)	1.372(4)	C(19)—O(3)	1.405(5)
C(9)—O(2)	1.416(4)	C(10)—O(2)	1.418(4)
C(7)—S(1)—C(8)	101.2(2)	C(11)—S(2)—C(12)	99.2(2)
O(4)—S(3)—O(6)	99.2(5)	C(18)—O(3)—C(19)	118.6(3)
C(1)—O(1)—C(22)	117.5(3)	C(9)—O(2)—C(10)	112.2(3)
C(7)—S(1)—C(8)—C(9)	72.1(3)	S(1)—C(8)—C(9)—O(2)	−170.0(3)
C(8)—C(9)—O(2)—C(10)	174.8(3)	O(2)—C(10)—C(11)—S(2)	−173.8(3)
C(10)—C(11)—S(2)—C(12)	81.1(3)	O(1)—C(22)—C(21)—O(6)	−87.4(6)
O(3)—C(19)—C(20)—O(4)	62.6(5)	O(6)—S(3)—O(4)—C(20)	87.0(7)



Scheme 1.



Scheme 2.

macrocycles were charactarized by NMR, mass spectrometry and elemental analysis. The structure of macrocycle **3** was confirmed by X-ray analysis.

Conductometric titration

In principle, measurements of the variation of electrical conductance with the concentration of metal salts and receptors can be used to assess the interactions taking place, determine the stoichiometry and stability constants of complex formation and to assess the nature of the interaction [24, 25]. We employed such measurements to establish stoichiometry of the complexes formed between several individual metal cations and ligands **1**, **2**, **3**, and to determine the stability constants of these complexes. The molar conductance versus $[L]_T/[M^{n+}]_T$ plot in acetonitrile at 25 °C is given in Figure 2 as an example. $[L]_T$ and $[M^{n+}]_T$ are the total concentrations of the ligand **2** and of the metal cation. As can be seen in Figure 2, the addition of oxathiacrown **2** to solutions of Ag^+ or Cu^{2+} but not of Cd^{2+} result in continuous decreases in the molar conductances of the resulting solutions. The decreases in molar conductances for Ag^+ and Cu^{2+} start to level off at a mole ratio of 1. The corresponding slopes of these plots for these cations also change at the point where oxathiacrown-to-cation mole ratio equals 1, implying the formation of 1:1 complexes. It is noteworthy that the stability constants of the oxathiacrowns-Ag^+ complexes of **2** and **3** are higher than those of oxathiacrowns-Cu^{2+} complexes

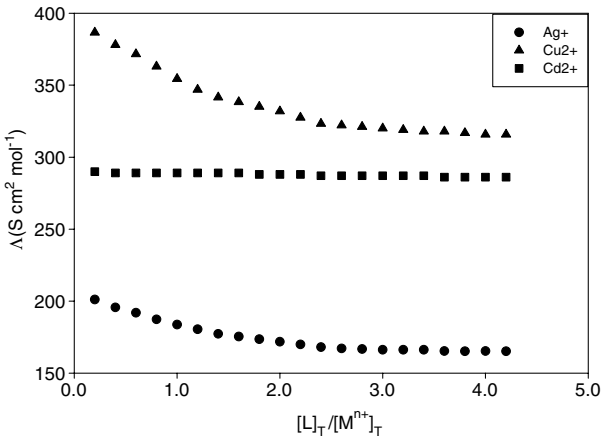


Figure 2. Conductance versus $[L]_T/[M^{n+}]_T$ for compound **2** with Ag^+, Cd^{2+} and Cu^{2+} in CH_3CN at 25 °C.

Table 3. $\log K_{assoc}$ (in $dm^3\ mol^{-1}$) for complexation of Cu^{2+} and Ag^+ with macrocycles **1**, **2** and **3** in acetonitrile at 25 °C.

Compound	Cu^{2+}	Ag^+
1		3.32 ± 0.06
2	4.38 ± 0.09	4.78 ± 0.11
3	3.68 ± 0.07	4.06 ± 0.08
I		4.34[a]
II	2.29 ± 0.04[b]	

[a]Reference [26]
[b]Reference [10].

(Table 3). Furthermore, it can also be seen that the strength of oxathiacrown **2**-Ag^+ and oxathiacrown **2**-Cu^{2+} complexes are higher than those for oxathiacrown **3**-Ag^+ and crown **3**-Cu^{2+} complexes.

For comparison purposes, the stability constants of 1,10-dithia-18-crown-6 (**I**) with Ag^+ and 1,4,8,11-tetrathia-14-crown-4 (**II**) with Cu^{2+} were incorporated (Table 3).

In conclusion, three new oxathiacrowns **1**, **2** or **3** have been synthesized in good yield. These receptors showed highest complexation ability and selectivity for Ag^+ and Cu^{2+} among all of the metal cations studied. Among these receptors, oxathiacrown **1** has the highest selectivity toward Ag^+. Therefore, ligand **1** can be used as good sensing agent for Ag^+ ions. A follow-up study on the other thermodynamic parameters and using them as sensing agents towards Ag^+ and Cu^{2+} will be reported in due course.

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