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Alexander T. Yordanov^a; Bruce R. Whittlesey^a; D. Max Roundhill^a

^a Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas, USA

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Communication

Lower Rim 2-Methylthioethoxy Substituted Calix[4]arenes as Shape Selective Complexants for Mercury and Silver

ALEXANDER T. YORDANOV, BRUCE R. WHITTLESEY and D. MAX ROUNDHILL

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, USA

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The compounds 5, 11, 17, 23-*tert*-butyl-25, 26, 27, 28-(2-methylthioethoxy)calix[4]arene 1 and 25, 26, 27, 28-(2-methylthioethoxy)calix[4]arene 2 have been synthesized from their corresponding 2-bromoethoxy derivatives. The crystal structure of 2 shows that the molecule has a flattened cone conformation. For the extraction of heavy metals from water into chloroform 1 and 2 show similar effectiveness for SnCl_3^- , PdCl_4^{2-} , PtCl_4^{2-} and AuCl_4^- , but for Hg^{2+} and Ag^+ , 2 is a better extractant than 1. This difference is discussed in terms of the relative hydrophobicities and structures of the two compounds

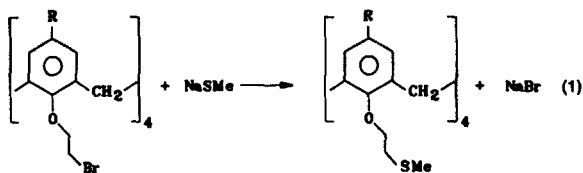
Keywords: Calix[4]arene, Mercury, Silver

INTRODUCTION

Recently we have shown that *N, N*-dimethyl-dithiocarbamoyl and thiolate substituted calix[4]arenes can be used as selective extractants for heavy metals [1]. These compounds effectively extract the ions Hg^{2+} , Pd^{2+} , Ag^+ and Au^{3+} from aqueous solution, but not Cd^{2+} , Ni^{2+} and Pt^{2+} . Since, however, these particular sulfur-

containing functionalities are potentially susceptible to hydrolysis and oxidation, we have begun seeking ligating groups that have higher aerobic stabilities but yet will retain the desired complexation selectivities for these and similar heavy metal ions. We have synthesized and characterized the two new 2-methylthioethoxy-substituted calix[4]arenes, 5, 11, 17, 23-*tert*-butyl-25, 26, 27, 28-(2-methylthioethoxy)calix[4]arene 1 and 25, 26, 27, 28-(2-methylthioethoxy)calix[4]arene 2 [2], and present data showing that they have novel selectivities for the extraction of mercury and silver from aqueous solution. These two derivatives both have the sulfur donor ligands on the lower rim, and differ only in whether they have hydrogen or *tert*-butyl substituents on the *para* positions of the upper rim. The chosen metal ions are ones that can potentially bind to the sulfur atom of a thioether group, [3] and also because they have commercial value if they can be recovered in pure form.

These two 2-methylthioethoxy derivatives have been synthesized by reacting the corre-



sponding 2-bromoethoxy compound with the methylthiolate anion (equation 1) [1, 4].

Compounds **1** (R=*tert*-Bu) and **2** (R=H) have been characterized by a range of analytical techniques including, for **2**, single crystal x-ray crystallography [5, 6]. The ^1H NMR spectrum of **1** shows a resonance for the methylthio group (δ 2.19s, CH_3S). The observation of a single sharp resonance for the *tert*-butyl groups supports the premise that **1** is in the cone conformation [7]. Compound **2** also shows resonances in ^1H NMR spectrum for the methylthio group (δ 2.17s, CH_3S ; 2.98t, CH_2S). The presence of two doublets for the ring methylenes (δ 3.17 d, 4H, CH_2 and 4.42 d, 4H, CH_2) is indicative of a cone conformation for **2**. By X-ray crystallography, **2** is found to have a flattened cone conformation. These compounds **1** and **2** with subtle but significant structural differences between them can potentially show different extraction properties for metal ions. Two features that may influence this extraction diversity between **1** and **2** are either their different hydrophobicities that results from the absence or presence of *tert*-butyl groups in the compounds, or their different complexation properties that may result from shape selectivity between the cone conformation of **1** and the flattened cone conformation of **2**.

We have used **1** and **2** as extractants for a series of heavy metals into chloroform from aqueous solution in order to determine whether a hydrogen or a *tert*-butyl group can cause these two compounds to have different extraction properties [8]. These data that are collected in the Table show that neither compound extracts tin or platinum from their chloride salts, [9] but that both **1** and **2** effectively extract gold. The most notable difference between the extraction

TABLE I Extraction of selected heavy metals by **1** and **2**

Metal Ion	% Extraction	
	Compound 1	Compound 2
SnCl_3^-	1	3
Hg^{2+}	6	62
Ag^+	65	97
PdCl_4^{2-}	70	63
PtCl_4^{2-}	0	0
AuCl_4^-	100	99

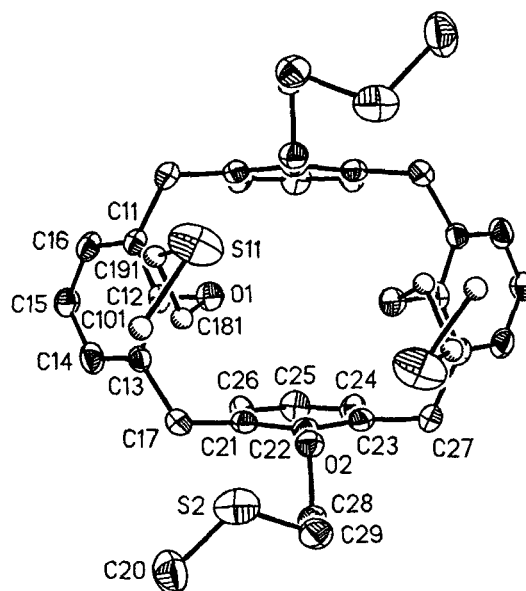


FIGURE 1 ORTEP Representation (30% Ellipsoids) of **2** Selected bond distances (Å) and angles ($^\circ$): C101–S11 1.87 (5), S11–C191 1.92(5), C191–C181 1.50 (6), C181–O1 1.46(4), C20–S2 1.81(1), S2–C29 1.79(1), C29–C28 1.48(1), C28–O2 1.439 (7), C20–S2–C29 100.8 (5), S2–C29–C28 116.5 (7), C29–C28–O2 108.9 (5), C28–O2–C22 112.8 (5), C101–S11–C191 94 (2), S11–C191–C181 115(4), C191–C181–O1 109(3), C181–O1–C2 111 (2).

data for **1** and **2** is the much higher extractability of Hg^{2+} by **2** as compared to **1**. An increase is also observed for Ag^+ , but the effect with this ion is smaller. From these data it is apparent that either **1** or **2** have comparable extraction properties (SnCl_3^- , PdCl_4^{2-} , PtCl_4^{2-} , AuCl_4^-), or that **2** is a better extractant than **1**. Since these data are for extraction into chloroform from an aqueous solution, it is to be expected that if boundary effects were the predominant factor leading to

this difference, the more hydrophobic compound would give the higher extractability. Since **1** with *tert*-butyl groups on the upper rim is expected to have the higher hydrophobicity, this compound is the one that should be the better extractant. The opposite result is observed.

Previous structural work on calix[4]resorcinarenes has shown that the H-substituted derivatives can form an elongated cone conformation, [10], and that calix[4]arenes adopt a pinched cone geometry, [11, 12] therefore we do not believe that this structure results from crystal packing forces. The structure of **2** shows such a flattened cone conformation with intramolecular O1...O1' and O2...O2' distances of 3.58 Å and 5.64 Å, respectively. This unsymmetrical structure correspondingly leads to a wide discrepancy between the transannular S11...S11' and S2...S2' distances. Such a ligand distortion can be advantageous to binding metal ions such as Hg²⁺ and Ag⁺ that readily adopt linear two-coordination, [13] thereby providing an explanation for our observation. Nevertheless we cannot exclude the possibility that other factors are involved in causing these changes in extraction selectivity between **1** and **2**.

Acknowledgements

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Supplementary Material Available

Tables of structure determination summary, atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, H-atom coordinates (8 pages).

References

- [1] Yordanov, A. T., Mague, J. T. and Roundhill, D. M. (1995). *Inorg. Chem.*, **34**, 5084.
- [2] Cobben, P. L. H. M., Egberink, R. J. M., Bomer, J. G., Bergveld, P., Verboom, W. and Reinhoudt, D. N. (1992). *J. Am. Chem. Soc.*, **114**, 10573.
- [3] Murray, S. G., Hartley, F. R. (1981). *Chem. Rev.*, **81**, 365.
- [4] Yordanov, A. T., Roundhill, D. M. and Mague, J. T. (1996). *Inorg. Chim. Acta*, **250**, 295.
- [5] Analytical and Spectroscopic data:- **1**: Anal. Calcd for C₅₆H₈₀O₄S₄: C, 71.1; H, 8.53; S, 13.6. Found: C, 71.0; H, 8.57; S, 12.5. ¹H NMR (CDCl₃): δ 1.05 (s, 36 H, *tert*-Bu); 2.19 (s, 12 H, CH₃S); 3.00–3.25 (m, 12 H, CH₂, CH₂S); 4.04 (t, 8 H, CH₂O); 4.36 (d, 4 H, CH₂); 6.77 (s, 8 H, ArH). ¹³C NMR (CDCl₃): δ 15.8 (q, ¹J(CH)=138.4 Hz, CH₃S); 28.8–35.2 (m, CH₂, CH₂S, CCH₃, CCH₃); 73.5 (t, ¹J(CH)=145.0 Hz, CH₂O); 125.1 (d, ¹J(CH)=153.2 Hz, ArCH); 133.6 (s, ArC); 144.9 (s, ArC); 152.8 (s, ArC). **2**: Anal. Calcd for C₄₀H₄₈O₄S₄: C, 66.6; H, 6.71; S, 17.8. Found: C, 67.0; H, 6.84; S, 17.6. ¹H NMR (CDCl₃): δ 2.17 (s, 12 H, CH₃S); 2.98 (t, 8 H, CH₂S); 3.17 (d, 4 H, CH₂); 4.04 (t, 8 H, CH₂O); 4.42 (d, 4 H, CH₂); 6.40–6.70 (m, 8 H, ArH). ¹³C NMR (CDCl₃): δ 15.8 (q, ¹J(CH)=138.1 Hz, CH₃S); 30.9 (t, ¹J(CH)=129.5 Hz, CH₂); 33.4 (t, ¹J(CH)=140.6 Hz, CH₂); 73.3 (t, ¹J(CH)=148.0 Hz, CH₂O); 122.5 (d, ¹J(CH)=162.8 Hz, ArCH); 128.3 (d, ¹J(CH)=155.4 Hz, ArC); 134.8 (s, ArC); 155.7 (s, ArC).
- [6] Crystallographic data for **2**: C₄₀H₄₈O₄S₄, M=721.0, monoclinic, space group C2/c, a=20.428(2) Å, b=10.581(1) Å, c=20.445(2) Å, β=118.461(5)°, V=3885.0 (8) Å³, Z=4, D_{calcd}=1.233 g cm⁻³, μ(MoKα)=2.83 cm⁻¹, R=0.077, R_w=0.104, GOF 1.31 for unique reflections with I ≥ 4.00 (I).
- [7] Because of some overlapping of the methylene hydrogens of the SCH₂ group with the ring methylenes, we cannot use the multiplicity of these latter hydrogens as an indication of the cone conformation; Gutsche, C. D., *Calixarenes*, Royal Society of Chemistry Cambridge, UK, 1989, p. 91.
- [8] The extraction procedures have been described in reference 1.
- [9] The failure of sulfur-derivatized calix[4]arenes to extract platinum has been explained on the basis of the kinetic inertness of PtCl₄²⁻; see Yordanov, A. T., Mague, J. T. and Roundhill, D. M., *Inorg. Chim. Acta*, 1995, **240**, 441.
- [10] Palmer, K. J., Wong, R. Y., Jurd, L. and Stevens, K. (1976). *Acta Crystallogr.* **B32**, 847.
- [11] Dahan, E. and Biali, S. E. (1991). *J. Org. Chem.*, **56**, 7269.
- [12] Conner, M., Janout, V. and Regen, S. L. (1991). *J. Am. Chem. Soc.*, **56**, 7269.
- [13] Biscarini, P., Fusina, L. and Nivellini, G. D. (1971). *Inorg. Chem.*, **10**, 2564.