

Calix[4]arenes with hard donor groups as efficient soft cation extractants. Remarkable extraction selectivity of calix[4]arene *N*-(X)sulfonylcarboxamides for Hg^{II}

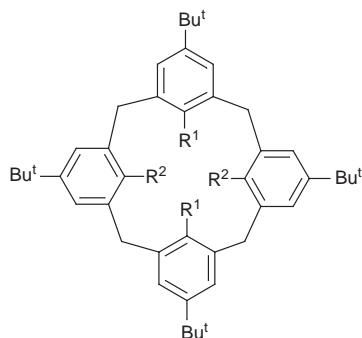
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Calix[4]arene *N*-(X)sulfonylcarboxamides efficiently extract Hg^{II} from acidic aqueous nitrate solutions with excellent selectivity over alkali, alkaline earth and many transition metal ions, including Pb^{II}, Ag^I and Pd^{II}.

Metal complexes of calixarene-based macrocyclic ligands are attracting ever-increasing attention,¹⁻³ especially for applications in metal ion separation processes. During the last decade, remarkable progress in the transition metal chemistry of calixarenes has been achieved.³ Recently, several papers have appeared which report utilization of calixarene derivatives in separations of soft heavy metal ions, *e.g.* Ag^I, Au^{III}, Pd^{II}, Pt^{II} and Cd^{II}.^{4,5} However, only very limited information on Hg^{II} extraction with calixarene-based ligands is available in the literature.⁵

Recently we synthesized new calix[4]arenes **1-4** with two



- 1 R¹ = OMe, R² = OCH₂C(O)NHSO₂CF₃
- 2 R¹ = OMe, R² = OCH₂C(O)NHSO₂Me
- 3 R¹ = OMe, R² = OCH₂C(O)NHSO₂Ph
- 4 R¹ = OMe, R² = OCH₂C(O)NHSO₂C₆H₄NO₂-4
- 5 R¹ = OBU, R² = OCH₂C(O)NHSO₂Ph
- 6 R¹ = OBU, R² = OCH₂CO₂H
- 7 R¹ = OBU, R² = OCH₂CO₂Et
- 8 R¹ = OMe, R² = OCH₂CO₂H
- 9 R¹ = R² = OMe
- 10 R¹ = R² = OH
- 11 R¹ = OBU, R² = OH

N-(X)sulfonylcarboxamide groups of 'tunable' acidity that exhibit good extraction selectivity for Pb^{II} over alkali and alkaline earth metal cations, as well as Cd^{II}, Co^{II}, Cu^{II}, Ni^{II} and Zn^{II}.⁶ However, these ligands failed to extract Pb^{II} in the presence of Hg^{II}.⁶ This unexpected favoring of a soft metal cation over a harder metal cation by ligands containing hard donor groups encouraged us to investigate the solvent extraction of Hg^{II}, Ag^I and Pd^{II} by **1-4** and related calix[4]arene derivatives **5-10** which have different pendant functional groups [*N*-(X)sulfonylcarboxamide, carboxylic acid, ester, ether, phenol]. To the best of our knowledge, this is the first report in which calixarene-type compounds without soft donor functions have been employed as Hg^{II} extractants.

The complexing abilities of calixarene-based ligands are known to vary significantly with alterations in their structures and conformations.² To study Hg^{II} extraction, we used the previously reported, conformationally mobile calix[4]arene *N*-(X)sulfonylcarboxamides **1-4**, as well as the related new compounds **5-7** which are restricted to the cone conformation. Calix[4]arene *N*-(X)sulfonylcarboxamide **5**‡ was prepared from the corresponding calixarene dicarboxylic acid **6**§ by the procedure described for the synthesis of **1-4**.⁶ We also utilized proton-ionizable calixarenes **8**⁸ and commercially available **10** which exist in cone conformations in CHCl₃ solution due to intramolecular hydrogen bonding, but may change into other conformations when converted into metal salts, and the conformationally flexible, non-ionizable derivative **9**⁹ which is predominantly the partial cone conformer in CHCl₃.¹⁰

Although all of the calixarenes **1-10** were found to extract Hg^{II} from acidic (pH 2.5) aqueous nitrate solutions into CHCl₃¶ to some degree, the metal loadings of the ligands are noted to vary markedly with their structures and functional group types (Fig. 1). The calix[4]arene *N*-(X)sulfonylcarboxamides **1-4** extract Hg^{II} most efficiently. Even though the 'tunable' acidity of the calixarene *N*-(X)sulfonylcarboxamides alters their extraction properties for harder metal cations,⁶ no significant difference in Hg^{II} loading was observed for **1-4** under the experimental conditions. For the conformationally flexible ligand **3**, the Hg^{II} loading was found to be considerably higher than that for analogue **5** which has a cone conformation. The calix[4]arene dicarboxylic acids **6** and **8** are weaker Hg^{II} extractants than the corresponding *N*-(X)sulfonylcarboxamides. The somewhat higher Hg^{II} loading for dicarboxylic acid **8** compared to **6** is ascribed to a greater conformational flexibility of the former. Conversion of calix[4]arene dicarboxylic acid **6** into the corresponding diester **7**, which also is restricted to the cone conformation, slightly reduces the level of Hg^{II} extraction. A conformational change from cone to partial cone is thought to be primarily responsible for the significant increase in Hg^{II} loading when the phenolic group in **10** was replaced with anisole units in **9**.

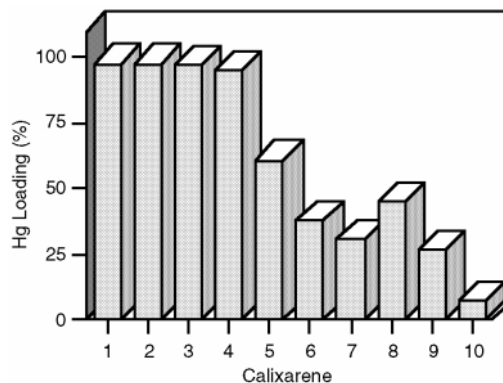


Fig. 1 Hg^{II} loading in extractions of 0.25 mM Hg^{II} from aqueous nitrate solutions at pH 2.5 into CHCl₃ with 0.25 mM calixarenes **1-10**

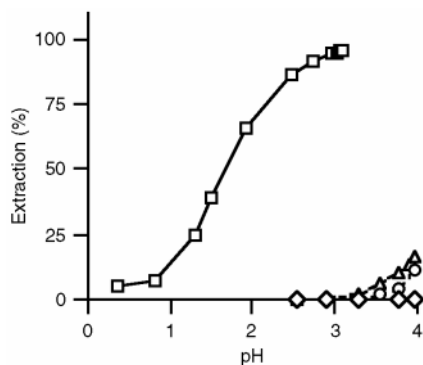


Fig. 2 pH profiles for Ag^{I} extraction from 1.00 mM aqueous AgNO_3 into CHCl_3 with 1.00 mM calix[4]arene *N*-(X)sulfonylcarboxamides **1–4**: (□) **1**, (◇) **2**, (○) **3** and (△) **4**

Coordination of Hg^{II} alters the UV spectra of calixarenes **1–10** in CHCl_3 . The absorption bands at 270–279 nm (for the substituted benzene rings) undergo hypsochromic shifts that are greatest for **1–4** (17–23 nm). Analogous spectral changes were not observed when CHCl_3 solutions of the ligands were contacted with 1.0 M NaOH. With Cl^- as the counterion instead of NO_3^- under otherwise identical conditions, Hg^{II} extraction was found to decrease dramatically for all of the calixarenes **1–10**.

Further investigation of the conformationally flexible calixarene *N*-(X)sulfonylcarboxamides **1–4** reveals extraction complex stoichiometries of two metal ions per ligand molecule. The extraction constants determined for ligands **1–4** vary as X is changed in the order: $\text{CF}_3 > \text{Me} > \text{Ph} > 4\text{-O}_2\text{NC}_6\text{H}_4$. This ordering differs from that found for Pb^{II} ,⁶ as well as alkali and alkaline earth metal cations, and indicates that the size rather than the electron-withdrawing ability of X is important in Hg^{II} extraction.

The results presented above suggest a significant contribution to the complex stability by π -interactions between Hg^{II} and the electron-rich aromatic rings in the calixarene framework. Previously, π -complexes of calixarenes with other soft heavy metal ions, Ag^{I} and platinum(II), have been reported.^{2,3,11}

The calix[4]arene *N*-(X)sulfonylcarboxamides **1–4** are also efficient Ag^{I} extractants from acidic and neutral solutions. Unlike Hg^{II} binding, the propensities of these ligands for Ag^{I} extraction are controlled by their acidities. Only ligand **1** extracts Ag^{I} at $\text{pH} < 3$, while a higher pH is required for weaker NH -acids **2–4** (Fig. 2). A similar trend is noted for extraction of Pd^{II} by **1–4**. Therefore, calixarene *N*-(X)sulfonylcarboxamides **2–4** are remarkably selective in Hg^{II} extraction from acidic (pH 2.0–2.5) nitrate solutions, since they efficiently extract Hg^{II} with negligible loadings of alkali, alkaline earth, and many transition metal cations, including Pb^{II} , Ag^{I} and Pd^{II} . Further investigation of soft metal ion separations with calix[4]arene *N*-(X)sulfonylcarboxamides is in progress.

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Notes and References

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‡ Selected data for **5**: yield 38%; mp 241–242 °C (Calc. for $\text{C}_{68}\text{H}_{86}\text{N}_2\text{O}_{10}\text{S}_2$: C, 70.68; H, 7.50; N, 2.42. Found: C, 70.74; H, 7.70; N, 2.28%); δ_{H} (200 MHz, CDCl_3) 0.85 (s, 18 H), 0.94 (t, *J* 7.1, 6 H), 1.25–1.44 (s + m, 22 H),

1.60–1.79 (m, 4 H), 3.21 (d, *J* 12.6, 4 H), 3.82–3.95 (m, 4 H), 4.33 (d, *J* 12.6, 4 H), 4.68 (s, 4 H), 6.54 (s, 4 H), 7.06 (s, 4 H), 7.42–7.72 (m, 6 H), 8.13–8.21 (m, 4 H), 10.41 (s, 2 H).

§ Synthesis of **6**: Calixarene **11**, prepared analogously to the dipropyl ether,⁷ was stirred at 80 °C with ethyl bromoacetate and NaH in dry DMF for 48 h. After evaporation of the solvent *in vacuo*, the residue was acidified with 1 M HCl and CH_2Cl_2 was added. The CH_2Cl_2 layer was evaporated *in vacuo* and the crude product was chromatographed on alumina with EtOAc–hexanes as eluent. Recrystallization from CH_2Cl_2 –MeOH gave the cone isomer of **7** as a white solid in 75% yield. Mp 195 °C (Calc. for $\text{C}_{60}\text{H}_{84}\text{O}_8$: C, 77.21; H, 9.01. Found: C, 77.51; H, 9.02%); δ_{H} (200 MHz, CDCl_3) 0.94–1.04 (s + t, 24 H), 1.17 (s, 18 H), 1.28 (t, *J* 7.1, 6 H), 1.36–1.55 (m, 4 H), 1.84–2.01 (m, 4 H), 3.17 (d, *J* 12.8, 4 H), 3.84 (t, *J* 7.4, 4 H), 4.20 (q, *J* 7.1, 4 H), 4.63 (d, *J* 12.8, 4 H), 4.83 (s, 4 H), 6.63 (s, 4 H), 6.90 (s, 4 H). Diester **7** was hydrolyzed to **6** by refluxing overnight with excess Me_4NOH in aq. THF. The THF was evaporated *in vacuo* and the residue was acidified with 6 M HCl. After extraction with CH_2Cl_2 , the solvent was evaporated *in vacuo* to give **6** as a white solid in 97% yield. Mp 243 °C (Calc. for $\text{C}_{56}\text{H}_{76}\text{O}_8 \cdot 0.2\text{CH}_2\text{Cl}_2$: C, 75.49; H, 8.61. Found: C, 75.33; H, 8.43%); δ_{H} (200 MHz, CDCl_3) 0.84 (s, 18 H), 0.94 (t, *J* 7.2, 6 H), 1.34 (s, 18 H), 1.23–1.42 (m, 4 H), 1.76–1.92 (m, 4 H), 3.29 (d, *J* 13.0, 4 H), 3.84–3.92 (m, 4 H), 4.24 (d, *J* 13.0, 4 H), 4.65 (s, 4 H), 6.56 (s, 4 H), 7.18 (s, 4 H), 11.34 (br s, 2 H). The presence of solvent in the analytical sample of **6** was evident in its ^1H NMR spectrum.

¶ Aqueous 0.25 mM Hg^{II} nitrate (pH 2.5, HNO_3) was extracted with a 0.25 mM calixarene solution in CHCl_3 . The Hg^{II} concentration in the aqueous phase was determined spectrophotometrically after extraction into CHCl_3 containing 14.0 ppm dithizone (λ_{max} 495 nm).

|| Aqueous 1.0 mM Ag^{I} nitrate (pH adjusted with HNO_3) was extracted with a 1.0 mM calixarene solution in CHCl_3 . The Ag^{I} concentration in the aqueous phase was determined by atomic absorption spectrophotometry.

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