Selective Chromogenic Reagents for Lead

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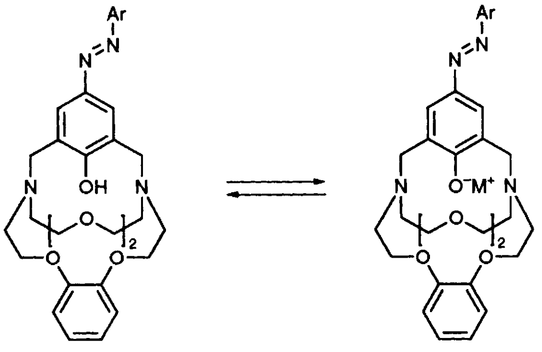
The cryptands **3** and **5** are both selective reagents for lead, they also respond to other doubly charged cations including Ca^{2+}, Sr^{2+} Hg^{2+} and Cd^{2+} but with significantly lower sensitivity; they show no significant response to Zn^{2+}, Cu^{2+} and Ba^{2+}.

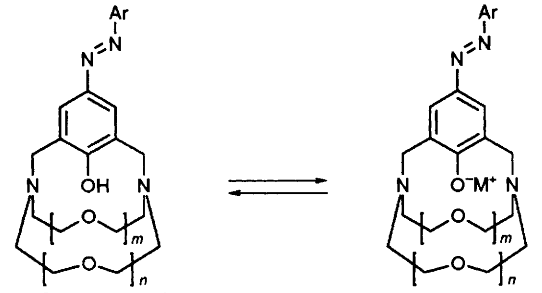
The cations Pb^{2+}, Cd^{2+} and Hg^{2+} are all highly toxic and because of their widespread use they can present serious environmental problems.[1] In particular there is a requirement for a reagent which will respond selectively to lead at low concentrations in, for example, water supplies and human blood. The classical chromogenic reagent for lead sensing is dithizone[2] which has adequate sensitivity but is not selective and is also susceptible to aerial oxidation. Because of our interest in reagents for sensing biologically important cations, we have developed[3] a number of chromogenic cryptands such as **1** which are potentially suitable for use in simple optical fibre based sensors.[4] Chloroform solutions of these compounds extract alkali metal cations from aqueous solution to form neutral cryptate salts such as **2** with a change in absorption spectrum that depends upon the size of the cation. Recently,[5] we described the cryptand **3** which is selective for Ca^{2+} because it apparently forms the stable ion pair **4** (M = Ca) which is extractable into an organic phase, this appears to be a consequence of the close permitted contact between anion and cation in **4**. This contrasts with the cryptand **1** which has a cavity of similar size but is highly selective for Na^+ rather than Ca^{2+} because its structure does not permit the close contact between anion and cation that is required for a stable ion pair analogous to **4**. These observations suggested that the cryptand **3** might form solvent soluble complexes with other doubly charged cations of a similar size to calcium. We report the results of an investigation of the behaviour of **3** and the analogous cryptand **5** as reagents for a range of cations.

Neither **3** nor **5** showed a significant response to small cations such as Zn^{2+} and Cu^{2+} in concentrations up to 10^{-2} and 10^{-3} mol dm^{-3}, respectively, at pH 7 but the cryptand **3** proved to be sensitive to Pb^{2+} in concentrations of 10^{-6} mol dm^{-3} at pH $\geqslant$ 6 and moderately sensitive to Cd^{2+} and Hg^{2+} at pH 7. The related cryptand **5** was also moderately sensitive to these doubly charged cations and responded to Pb^{2+} in concentrations of 10^{-6} mol dm^{-3} at pH 7. Details of absorbance and extraction coefficients are recorded in Table 1, the absorbance of the complexes is consistent with ion paired species analogous to the Ca^{2+} complex described previously.[5] Table 1 also includes data for alkali metal cations taken from earlier work[3,5] since these cations may be present in both water and blood samples, and for comparison data is also reported for Sr^{2+} but response to Ba^{2+} was too weak to give reliable data.

The results reported in Table 1 for cryptands **3** and **5** are difficult to rationalise simply in the terms of cation radius (r)[6] and charge, and the dimensions of the cryptand cavities. In particular we note that in both cases Ca^{2+} (r = 100 pm) is complexed more strongly than Sr^{2+} (r = 116 pm) and Ba^{2+} (r = 136 pm) but that Pb^{2+} (r = 118 pm) is complexed more strongly than Hg^{2+} (r = 102 pm) and Cd^{2+} (r = 95 pm). This appears to be a consequence of the greater affinity of Hg^{2+} and Cd^{2+} for nitrogen ligands and Pb^{2+} for oxygen ligands which has been demonstrated in earlier work[7] with [2.2.2]cryptands. In most cases cryptand **3** binds doubly charged cations more strongly than cryptand **5** in accord with the greater ability of the former to provide good contact between the metal cation and the accompanying anion in the organic phase. We also note that the phenolic cryptand **6** has



1 **2**



3 m = 1, n = 3
5 m = n = 2

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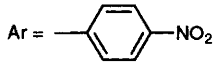

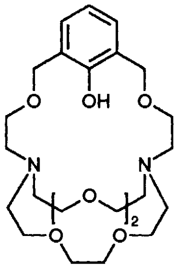

6

Table 1 Extraction coefficients and selectivities

Cation	$Log_{10}K_e$[a,c] (λ/nm)	
	3	**5**
Na^+	−8.5[b] (544)	−6.6[b] (554)
K^+	−9.3[b] (538)	−9.3[b] (554)
Ca^{2+}	−5.7[b] (480)	−7.8[b] (500)
Sr^{2+}	−7.2 (488)	
Pb^{2+}	−0.3 (466)	−1.2 (488)
Cd^{2+}	−2.6 (476)	−4.7 (482)
Hg^{2+}	−3.7 (448)	−3.5 (468)

[a] For a solution of **3** or **5** at *ca.* 10^{-5} mol dm^{-3} in $CHCl_3$, and solutions of metal chlorides at 10^{-6}–1 mol dm^{-3} in water, using a tris(hydroxymethyl)methylamine–HCl buffer. K_e is based on changes in absorption at the wavelength/nm given in parentheses. [b] Taken from refs. 3 and 5. [c] $K_e = [H^+]_{aq}[M^+Cl^-]_{org}/[M^+]_{aq}[ClH]_{org}$ for Na^+ and K^+, $K_e = [H^+]_{aq}[MCl^+Cl^-]_{org}/[M^+]_{aq}[ClH]_{org}$ for M^{2+} salts.

been reported[8] to bind both Cu^{2+} and Pb^{2+} very strongly in aqueous solution but **3** and **5** have only very low affinity for Cu^{2+}, this may reflect the inability of these cryptands to adapt to the steric requirements of the smaller Cu^{2+} cation (r = 72 pm)[9] or the different conditions for measurement. The much higher sensitivity of cryptands **3** and **5** for Pb^{2+} than for any of the other cations studied indicates their potential as reagents for use in optical sensors for lead salts in neutral or basic aqueous solution in the concentration range 10^{-8} to 10^{-4} mol dm^{-3}. However, the relatively low absorbance of the azophenol chromophore (ε *ca.* 10^4) would require the use of a solution of the reagent in a very small quantity of the organic phase which is best done by using an optical fibre sensor of a type which has been described in an earlier publication.[4] We also note that the differing selectivities of the two closely related reagents **3** and **5** would provide a dual probe sensor with selectivity suitable for measurements of lead concentrations in both environmental and biological samples.

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