Macroheterocycles; XX. Synthesis of Cryptands Containing Urea and Thiourea Moieties

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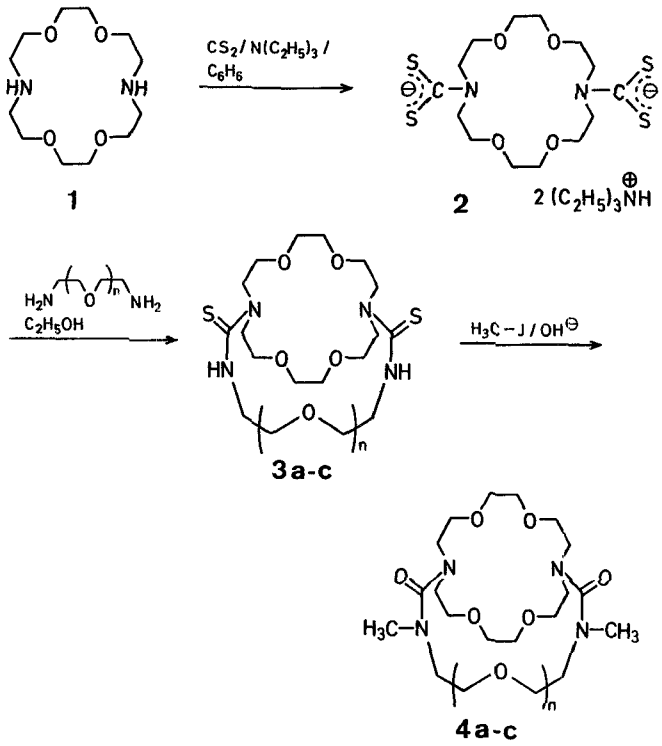
The complexation tendencies and unusual selectivities shown by cryptands can be modified by structural and environmental changes on the cryptands. These properties should lead to a number of possibilities to obtain practically important compounds.

We now describe the synthesis of novel cryptands containing urea and thiourea moieties. The reaction of diaza-18-crown-6 **(1)** with carbon disulfide in benzene in the presence of triethylamine resulted in dithiocarbamate salt **(2)**, which was subsequently refluxed in ethanol with polyoxyethylenediamines to give cryptands **(3)**.



The reaction was carried out until no more evolution of hydrogen sulphide was observed. Compounds **4a–c** were prepared from cryptands **3a–c** and methyl iodide under conditions of phase-transfer catalysis according to the procedure we described previously for monocyclic compounds[1].

The ion selectivity of cryptands **3** was evaluated using liquid membrane electrodes (chloroform/cryptand **3**)[2]. Cation-selectivity of cryptands **3** towards alkali metal ions is unusual in comparison with ordinary cryptands. The following selectivity sequences for compounds **3a–c** were found:

3a:	$K > NH_4 \approx Cs \gg Li > Na > Rb$	$Ba \gg Sr \gg Ca > Mg$
3b:	$NH_4 > Rb \approx Li > Na \approx Cs \approx K$	$Ba \gg Sr > Ca > Mg$
3c:	$NH_4 > Rb > Cs \approx Na > K > Li$	$Ba > Sr > Ca > Mg$

Cryptands 3; General Procedure:

Diaza-18-crown-6 (**1**; 10.41 g, 0.04 mol) is dissolved in benzene (50 ml) at 50°C. To this solution triethylamine (8.10 g, 0.08 mol) and carbon disulfide (6.09 g, 0.08 mol) in benzene (20 ml) are added in the given order with stirring. When the addition is complete, stirring is continued for 15 min. Then the mixture is cooled to room temperature, the precipitate is filtered off, washed with benzene (20 ml) and dried; yield of salt **2**: 21.11 g, (93%); m.p. 135–137°C (dec.). Salt **2** is used in the next step without further purification.

The corresponding polyoxyethylenediamine is added with stirring to a suspension of dithiocarbamate salt **2** in ethanol (1.8 l) and the mixture is refluxed with stirring under an inert gas. After 20 h, when the evolution of hydrogen sulphide has ceased, the ethanol is removed under reduced pressure. Cryptands **3a–c** are purified by chromatography (silica gel, chloroform/methanol 10:1 as eluent) and recrystallized from acetone.

Cryptands 4; General Procedure:

50% Aqueous sodium hydroxide (12 mmol) is added to a suspension of the corresponding cryptand **3** (2 mmol) and benzyltriethylammonium chloride (5% mol) in methyl iodide (5 ml) and the mixture is heated under reflux with vigorous stirring for 6 h. The aqueous layer is separated and extracted with chloroform (3 × 15 ml). The organic layer and extracts are combined, dried with anhydrous magnesium sulfate, and the solvent is removed under vacuum. Cryptands **4a–c** are purified by chromatography on silica gel with chloroform/methanol (10/1) as eluent.

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[1] A. V. Bogatsky, N. G. Lukyanenko, T. I. Kirichenko, *Synthesis* **1982**, 464.

[2] J. Petranek, O. Ryba, *Tetrahedron Lett.* **1977**, 4249.

Table. Cryptands **3a–c** and **4a–c** prepared

Product No.	n	Yield [%]	m.p. [°C]	Molecular Formula[a]	M.S. *m/e* (M^+)	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
3a	1	11	173–175°	$C_{18}H_{34}N_4O_5S_2$ (450.7)	450	3.63 (m, 32H); 7.45 (t, 2H, J = <3.0 Hz)
3b	2	20	183–184°	$C_{20}H_{38}N_4O_6S_2$ (494.7)	494	3.68 (m, 36H); 7.81 (t, 2H, J = 3.87 Hz)
3c	3	12	122–123°	$C_{22}H_{42}N_4O_7S_2$ (538.8)	538	3.63 (m, 40H); 7.75 (t, 2H, J = 4.37 Hz)
4a	1	81	99–101°	$C_{20}H_{38}N_4O_7$ (446.6)	446	2.80 (s, 6H); 3.48 (m, 32H)
4b	2	82	oil	$C_{22}H_{42}N_4O_8$ (490.7)	490	2.80 (s, 6H); 3.50 (m, 36H)
4c	3	85	oil	$C_{24}H_{46}N_4O_9$ (534.7)	534	2.77 (s, 6H); 3.48 (m, 40H)

[a] *Satisfactory microanalyses obtained: C ±0.32, H ±0.28, N ±0.22.*