Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **11**: 115–119, 1991.

Silver Selective Benzimidazol-2(1*H*)-one Based, Sulphur-Containing Podands

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(Received: 7 August 1990; in final form: 8 April 1991)

Abstract. Podands based on benzimidazol-2(1*H*)-one, containing S and terminal NH_2 groups, selectively transport and extract silver picrate over Mg^{2+}, Ca^{2+}, Sr^{2+}, Pb^{2+} and Tl^{+} picrates.

Key words. Benzimidazol-2-(1*H*)-one, podands, cation picrates, extraction, transport, selectivity.

1. Introduction

The significance of podands as ionophores across apolar membranes has been emphasized due to the ease with which they can be synthesized and the faster rates of complexation and decomplexation which they display, in comparison with macrocyclic systems [1]. However, podands possessing a heterocyclic urea moiety, which has demonstrated its pre-eminent contribution in the design of preorganised macrocyclic hosts, have been much less frequently studied [2, 3]. Thus, we have designed a benzimidazol-2(1*H*)-one based podand, model structure 1, with the possibility of incorporation of a varied number and combination of heteroatoms, two or three carbon interceptions between heteroatoms and the limited degree of freedom favoring the formation of a pseudocavity. The CPK model of **1**($n = 1, m = 0, x = S$) exhibits a spherical pseudocavity of heteroatoms but in its analog ($n = 2$), the urea oxygen moves inwards and the cavity acquires an oval shape. The presence of additional heteroatoms in the chain could further augment the ligating potential of these podands. Here, we have initially chosen to synthesize podands **1** possessing O, S and terminal NH_2 and to study their extraction and transport nature through a chloroform layer towards soft Ca^{2+}, Mg^{2+}, Sr^{2+}, Tl^{+}, Ag^{+} and Pb^{2+} picrates.

2. Experimental

Benzimidazol-2(1*H*)-one with 1,2-dibromoethane (excess) under solid–liquid phase transfer catalysis conditions (solid NaOH–TEBA) at 80–100°C gave dibromides **2a**, m.p. 105–108°C and **3a**, m.p. 180–185°C in 53 and 8% yields, respectively. Similarly, benzimidazol-2(1*H*)-one with 1,3-dibromopropane (3 equiv.) gave **2b**, liquid (20%), **3b**, m.p. 65–75°C (22%), **3c**, m.p. 98–100°C (18%) and **3d**, m.p. 122–125°C (10%). Compound **2a** on refluxing with thiophenol and *o*-aminothiophenol in ethanol/KOH gave **4c**, liquid (55%) and **4a**, liquid (60%), respectively.

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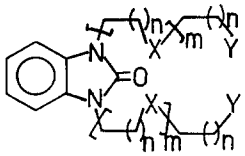
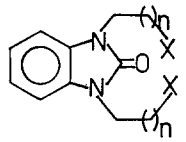


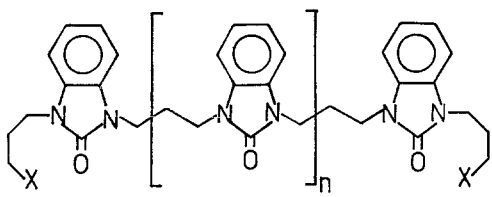
(1)

n=1,2
m=0,1
X= O,N,S, etc.
Y= NH_2, etc.



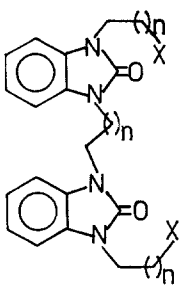
(2) a; n=1, X=Br
b; n=2, X=Br

(4) a; n=1, X= SC_6H_4-NH_2-o
b; n=2, X= SC_6H_4-NH_2-o
c; n=1, X= SC_6H_5



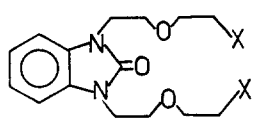
(3c) n=1

(3d) n=2



(3) a; n=1, X=Br
b; n=2, X=Br

(5) a n=1 X= SC_6H_4-NH_2-o
b n=2 X= SC_6H_4-NH_2-o



(6) X= Br

(7) X= SC_6H_4-NH_2-o

Table I. Extraction [6] ($\times 10^3$ ratio of metal picrate over podand in organic layer) and transport [7] rates ($\times 10^8$ moles/24 h)* of podands **4a–c**, **5** and **7**‡

Podand	Mg^{2+}	Ca^{2+}	Sr^{2+}	Tl^{+}	Ag^{+}	Pb^{2+}	Selectivity Ratios		
							Ag^{+}/Sr^{2+}	Ag^{+}/Tl^{+}	Ag^{+}/Pb^{2+}
4c	3.6	3.33	37	7.95	457	32.5	12.4	56.3	14.1
	(15)	(1)	(15)	(3)	(52)	(27)	(3.5)	(17.3)	(1.9)
4a	4.7	7.1	53.5	7.4	622	73	11.7	8.4	8.5
	(12)	(12)	(43)	(19)	(314)	(47)	(7.3)	(16.5)	(6.7)
4b	18.6	15.8	115	32.5	259	120	2.3	8.1	2.2
	(45)	(50)	(77)	(41)	(249)	(72)	(3.2)	(6.1)	(3.5)
5b	10.8	10.5	–	20.8	359	139	–	13.3	2.5
	(208)	(181)	(368)	(377)	(391)	(236)	(1.10)	(1.0)	(1.7)
7	10	10	69	11.4	771	123	11.2	550	6.3
	(36)	(40)	(37)	(41)	(200)	(65)	(5.4)	(4.9)	(3.1)

*Values in parenthesis pertain to transport rates and other data correspond to extraction constants.

‡Extraction conditions: 0.01M metal picrate in water and 0.01M ligand in chloroform. Transportation conditions; Aqueous phase I, 0.001M picrate in water (3mL); organic phase, 0.001M ligand in chloroform (15 mL); aqueous phase II, water (9 mL).

Similarly, **2b**, **3a** and **3b** with *o*-aminothiophenol gave podands **4b**, liquid (65%), **5a**, m.p. 175–180°C (60%) and **5b**, liquid (52%), respectively [4].

3. Results and Discussion

Podand **4c**, possessing three ligating sites (O and 2S), extracts [5] Ag^+ picrate in chloroform nearly 12 and 14 times better than similar sized Sr^{2+} and Pb^{2+} picrates and 56 times better than Tl^+ picrate (see Table I). It does exhibit selectivity in transport across a chloroform layer towards Ag^+ but not of the same order as the extraction. The podand **4a**, with five ligating sites (O, 2S, $2NH_2$) has an enhanced extraction and transport character towards Mg^{2+}, Ca^{2+}, Sr^{2+}, Tl^+, Ag^+ and Pb^{2+} compared to **4c**, demonstrating the positive contribution of terminal primary amino groups in complexation. Its extraction selectivity towards Ag^+ against Sr^{2+}, Pb^{2+}, and Tl^+ is marginally lowered but its transport selectivity towards Ag^+ is, in general, increased to 7.3, 16.5 and 6.7 times, respectively [7]. Evidently, both **4c** and **4a** are selective ionophores for Ag^+.

The podand **4b**, possessing two propylene spacer groups between sulphur and the benzimidazole N, accomplishes an overall increase in extraction and transport of metal picrates compared to **4a** except for Ag^+, where a decrease is noticed in both characteristics. Podand **5b**, with one more ligating heteroatom than **4b** and an additional benzimidazolone ring, constitutes a relatively wide mouthed cavity and shows a decrease in extraction but a remarkable increase in transport rates devoid of any conspicuous selectivity. The increase in entropy of the ligand decreases the extraction character but the increase in decomplexation enhances the transport rates.

Since, ethylene bridges between S and benzimidazolone and the presence of terminal primary amines in these podands led to better selectivity of transport towards Ag^+, an increase in the number of heteroatoms and in the size of the pseudocavity was planned. Podand **7** has been synthesized by the condensation of *o*-aminothiophenol with **6**, which in turn has been obtained by the reaction of benzimidazol-2(1*H*)-one with *bis*(2-bromoethyl) ether. Compound **7** shows relatively enhanced extraction and transport values towards metal picrates compared to **4a**. It extracts and transports Ag^+ over Pb^{2+}, Tl^+, Sr^{2+}, Ca^{2+} and Mg^+ with more selectivity than observed in ligands with propylene bridges (**4b** and **5b**) but with lower selectivity than **4a**.

Thus, it is found that these benzimidazol-2-(1*H*)-one based podands containing O and S heteroatoms with terminal NH_2 groups extract and transport Ag^+ picrate selectively compared to Pb^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Tl^+ picrates, and this selectivity is further favoured by ethylene bridges between S and benzimidazol-2(1*H*)-one rather than propylene bridges. Further investigations on the effect of combination of O, N, S and the presence of an ethylene urea moiety in the backbone of model podand **1** are being carried out.

Acknowledgement

We thank DST, New Delhi for financial assistance. COSIST and SAP assistance of UGC, New Delhi is also acknowledged.

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4. All compounds give satisfactory spectral and mass and/or analytical (in case of solids) data.
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