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### Amide-armed Azamacrocycles as a New Series of Synthetic Carriers for Alkali and Alkaline Earth Metal Cations

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Novel azamacrocycles having amide-functionalized arm groups have been shown to mediate selective and efficient transport of 'hard' alkali and alkaline earth metal cations *via* three-dimensional complexations, while the parent azamacrocycles favour 'soft' metal cations.

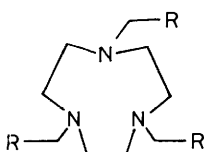
Armed macrocyclic host molecules, characterized by parent macrocyclic ligands and flexible cation-ligating arm groups, have attracted much attention.<sup>1</sup> They form three-dimensional but kinetically labile complexes with several metal cations, and mediate effective transport of them.<sup>2-4</sup> Since their cation-binding and transport properties are essentially controlled by the natures of the macrocyclic skeletons and ligating side-arms, structural combinations suitable for new and specific carriers can be designed.

Here we report the remarkable cation-binding and transport properties of amide-armed azamacrocycles. Parent azamacrocycles are known to act as powerful ligands for 'soft' transition

**Table.** Cation transport profiles of amide-armed macrocycles and related carriers<sup>a</sup>

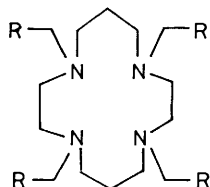
Carrier	Transport rate $\times 10^6$ (mol h <sup>-1</sup> )						
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cs <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Ba <sup>2+</sup>
(1)	2.5	1.4	*	*	*	1.9	2.4
(2)	*	*	*	*	*	*	*
(3)	1.4	0.8	*	*	*	*	8.9
(4)	*	*	*	*	*	*	*
(5)	*	*	*	*	*	*	*
(6)	1.5	4.3	7.0	2.2	*	1.9	0.6
(7)	0.8	6.5	1.2	1.4	*	0.4	3.7

<sup>a</sup> Transport conditions; Aq. I: Guest perchlorate, 0.50 mmol/H<sub>2</sub>O, 5 ml. Membrane: Carrier, 0.0372 mmol/CHCl<sub>3</sub>, 12 ml. Aq. II: H<sub>2</sub>O, 5 ml. Initial transport rates of guest cations were indicated. \* Below limit of detection ( $<0.3 \times 10^{-6}$  mol h<sup>-1</sup>).



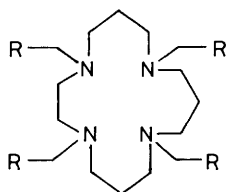
(1) R = CONEt<sub>2</sub>

(2) R = CO<sub>2</sub>Et

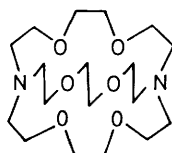


(3) R = CONEt<sub>2</sub>

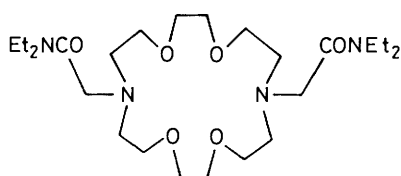
(4) R = CO<sub>2</sub>Et



(5) R = CONEt<sub>2</sub>



(7)

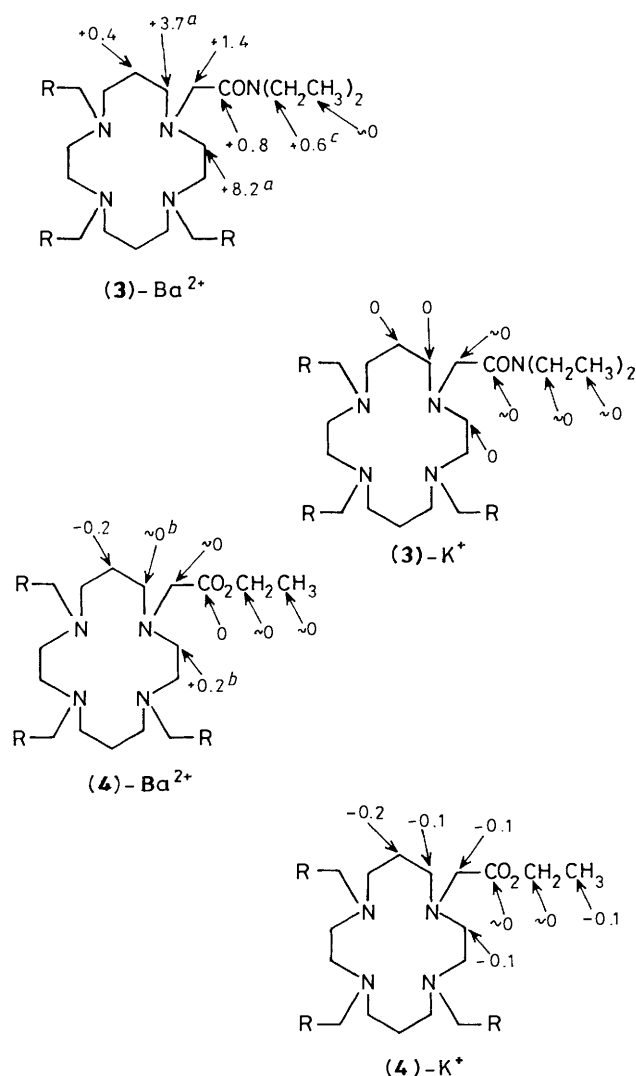


(6)

metal cations,<sup>5</sup> but we found that some amide-armed azamacrocycles specifically formed encapsulated complexes with 'hard' Ba<sup>2+</sup> and Li<sup>+</sup> ions and effectively transported them. Since their guest-selectivities were rather different from those of simple azamacrocycles, crown- and cryptand-type carriers, the present study provides a new series of host compounds exhibiting selective transport abilities for alkali and alkaline earth metal cations.

We prepared a series of amide- and ester-armed azamacrocycles (1)–(5) having 9-, 14-, and 15-membered rings from the corresponding polyamine macrocycles and alkyl chlorides, and compared their transport properties with those of the amide-armed crown ether (6)<sup>6</sup> and the bicyclic cryptand (7). The liquid membrane transport of various metal perchlorates was achieved in a U-tube glass cell (2.0 cm, i.d.) as described previously,<sup>3</sup> the transported amounts of guest cations and co-transported ClO<sub>4</sub><sup>-</sup> anion being individually determined by atomic absorption and ion-selective electrode techniques.

Amide-armed azamacrocycle (3) transported Ba<sup>2+</sup> ion effectively, but failed to do so for K<sup>+</sup> and Na<sup>+</sup> ions though they are of similar ion-sizes (see Table). Since ester-armed azamacrocycle (4) could not act as a carrier for any of the alkali and alkaline earth cations examined, introduction of an amide-functionalized arm into the azamacrocyclic skeleton significantly enhanced the transport ability for the hard Ba<sup>2+</sup> cation. In contrast, the crown ether (6) and the cryptand (7) carried Na<sup>+</sup> and/or K<sup>+</sup> ions more effectively than Ba<sup>2+</sup> ion,



**Figure.** Ba<sup>2+</sup>- and K<sup>+</sup>-induced changes in <sup>13</sup>C n.m.r. chemical shift of the armed azamacrocycles (3) and (4) (p.p.m.). Conditions: azamacrocycle (0.050 mmol), Ba(ClO<sub>4</sub>)<sub>2</sub> or KClO<sub>4</sub> (0.050 mmol), MeCN-D<sub>2</sub>O (4:1) (1.0 ml). <sup>a,b</sup> These signals could not be unequivocally assigned. <sup>c</sup> Calculated from the averaged values of two signals.

and selective transport of the latter ion was not achieved with these conventional carriers. The moderate transport efficiency of the amide-armed triazamacrocycle (1) for Li<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and Ba<sup>2+</sup> ions contrasted with that of the tetra azamacrocycle (5) for which it was very low. Thus, the cation transport profile of these amide-armed azamacrocycles is clearly dependent on the ring-size of the parent azamacrocycle as well as the nature of the ligating side-arm group.

The cation-binding properties of the azamacrocycles (3) and (4) were investigated by <sup>13</sup>C n.m.r. spectroscopy (see Figure).

Thus, addition of Ba(ClO<sub>4</sub>)<sub>2</sub> (1 mol equiv.) to the amide-armed azamacrocycle (3) solution led to significant spectral changes upon complexation,\* whereas KClO<sub>4</sub> induced no spectral change. Since the signals for the carbons on both the amide arm and the polyamine ring of the azamacrocycle (3) shifted considerably, it is suggested that co-operative action of the amide-arm and parent polyamine ring led to the selective and complete inclusion of the guest Ba<sup>2+</sup> ion.† The <sup>13</sup>C n.m.r. spectrum of the ester-armed azamacrocycle (4) was only slightly changed in the presence of Ba<sup>2+</sup> or K<sup>+</sup> cations, indicating that no stable complexation occurred. These results clearly revealed that a combination of an amide-functionalized arm and an azamacrocyclic skeleton offered selective three-dimensional complexations as well as unique and efficient transport for hard metal cations.‡ Further variation of the arm-donor group and parent macrocyclic ligand may provide new possibilities in design of specific ligands and/or carriers for a new series of guest cations.§

### Acknowledgements

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\* <sup>13</sup>C N.m.r. spectral changes supported 1:1 complexation between the azamacrocycle (3) and Ba<sup>2+</sup> ion.

† 1,4,7,10-Tetrahydroxyethyl-1,4,7,10-tetra-azacyclododecane is known to accommodate a three-dimensional cavity for guest cation.<sup>7</sup>

‡ Some amide-containing acyclic and cyclic host molecules have recently been characterized.<sup>8</sup>

§ Several types of armed azamacrocycles form characteristic encapsulated complexes with 'soft' transition metal cations.<sup>9</sup>