



Dendritic effects of crown ether-functionalized dendrimers on the solvent extraction of metal ions

Dimitrios Alivertis, Georgios Paraskevopoulos, Vassiliki Theodorou, Konstantinos Skobridis *

Department of Chemistry, University of Ioannina, GR-451 10 Ioannina, Greece

ARTICLE INFO

Article history:

Received 15 March 2009

Revised 29 July 2009

Accepted 14 August 2009

Available online 21 August 2009

ABSTRACT

The ability of a series of crown ether-functionalized dendrimers to function as alkali metal picrate extraction agents is assessed by liquid–liquid extraction and ^1H NMR titration experiments. Crown ether-functionalized dendrimers that contain Fréchet-type poly(benzyl ether) dendrons of different generation as building blocks display different extraction characteristics toward alkali metal cations. Positive and negative dendritic effects depending on the generation of the dendrimer are assigned in the complexation behaviour of the dendritic host compounds.

© 2009 Elsevier Ltd. All rights reserved.

Host–guest chemistry has been a central concern in the field of supramolecular chemistry. The design and construction of hosts that are capable of selective binding of guest molecules require precise control over geometrical features and interaction complementarity. This can be achieved by using versatile building blocks that allow the introduction of binding sites with directional binding interactions at well defined positions.¹ Since the discovery of crown ethers and their ability to form stable host–guest complexes with metal ions,² host–guest chemistry has moved from simple macromonocyclic complexes³ to more sophisticated structures⁴ involving lariat-type complexes,⁵ macrooligocyclic cryptands,⁶ rigid spherands,^{1a,7} and other supramolecular systems.⁸ A particular host family are functional dendrimers that are distinguished by the use of covalently attached active core molecules, especially those based on macrocyclic cores. The many results reported so far have led to an attractive new branch of supramolecular chemistry,⁹ which includes a variety of receptors, such as dendritic porphyrins, dendroclefts and dendrophanes, that show specific properties.¹⁰

The highly branched nature of dendrimers and the presence of a large number of surface groups (inherent of a dendritic skeleton) result in several special effects, known as the ‘dendritic effect’.¹¹

In a previous publication we reported the synthesis and characterisation of a series of novel dendritic host compounds **1–9**, containing crown ether moieties of different ring sizes as the core unit, surrounded by Fréchet-type poly(benzyl ether) wedges of first, second or third generation (Fig. 1).¹² Actually, in this series of compounds the crown ether ring sizes systematically varied from benzo-12-crown-4 via benzo-15-crown-5 to benzo-18-crown-6. The motive for the synthesis of this particular type of crown ether-functionalized dendrimers was to highlight the com-

petition between multiplicity and cooperativity effects of a neighbouring macrocyclic ring and dendritic branches of first, second or third generation, comprising 6, 14 or 30 oxygen atoms as potential metal ion coordination sites. Furthermore, the incorporation of the Fréchet-type dendritic moieties confers rigidity and lipophilicity upon the resulting crown ethers, factors which have been shown to affect the selectivity and the binding avidity of host systems.

We report here the specific cation-binding properties of the dendritic host compounds **1–9** as evaluated from picrate extraction experiments. In addition, ^1H NMR spectra were recorded to assess the influence of the steric and electronic factors of the Fréchet-type dendritic wedges on the complexation properties of the present host compounds.

In order to establish the extent of the dendritic effects on the complexation properties, it was necessary to make a comparison with the corresponding parent crown compounds.

The alkali metal cation (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) complexing abilities of the crown ether-functionalized dendrimers **1–9** and of benzo-12-crown-4, benzo-15-crown-5 and benzo-18-crown-6 ethers were assessed by solvent extraction of aqueous alkali metal picrates with dichloromethane solutions of the above compounds. The percent extractabilities (%Ex), defined as percent picrate extracted into the organic phase, are shown in Table 1.

Considering the common size relationships between cation diameter and crown ring interior, the observed extractabilities are reasonable. The dendrimers are shown to extract alkali metal ions in a generation-dependent manner. The results indicate, in general, an increase of the extraction efficiencies for the alkali metal cation from the crown ether model compounds to the first generation dendrimers, and a gradual decrease of extraction efficiencies from the first generation via second to third generation crown ether-functionalized dendrimers. In other words, positive and negative dendritic effects are notable in the complexation

* Corresponding author. Tel.: +30 26510 08598; fax: +30 26510 08670.
E-mail address: kskobrid@cc.uoi.gr (K. Skobridis).

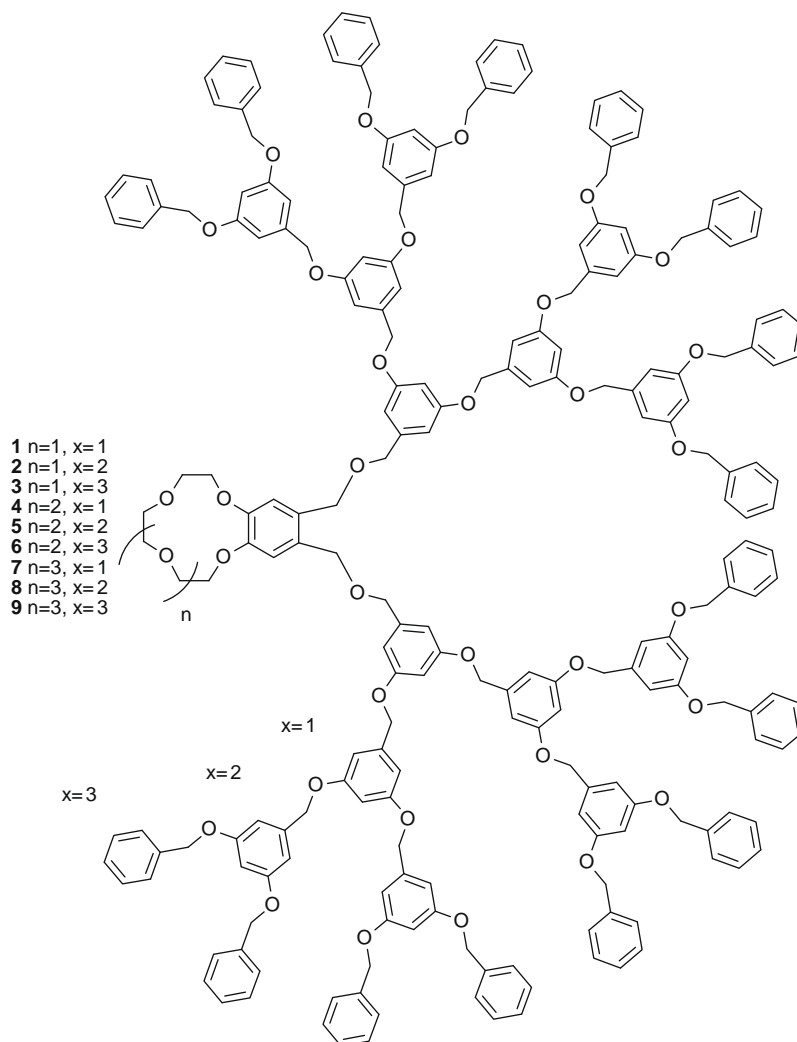


Figure 1. Formulae of crown ether-functionalized dendrimers 1–9.

Table 1
 Results of liquid–liquid alkali metal extraction experiments^a

Host	Percentage of picrate extracted ^b (%)				
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
Benzo (12-crown-4)	1.5 ± 0.3	1.3 ± 0.1	0.9 ± 0.2	0.7 ± 0.1	0.7 ± 0.1
1	2.3 ± 0.1	1.7 ± 0.2	1.1 ± 0.1	1.1 ± 0.2	0.9 ± 0.2
2	1.6 ± 0.2	1.5 ± 0.1	1.1 ± 0.2	0.8 ± 0.2	0.5 ± 0.1
3	0.9 ± 0.1	0.9 ± 0.2	1.0 ± 0.2	0.6 ± 0.2	0.5 ± 0.2
Benzo (15-crown-5)	1.2 ± 0.2	3.5 ± 0.3	4.7 ± 0.2	2.9 ± 0.1	1.6 ± 0.3
4	1.5 ± 0.1	5.1 ± 0.2	5.6 ± 0.2	3.3 ± 0.1	1.4 ± 0.2
5	0.9 ± 0.2	3.7 ± 0.4	4.4 ± 0.1	3.2 ± 0.2	1.0 ± 0.3
6	0.5 ± 0.1	1.9 ± 0.2	3.4 ± 0.1	2.0 ± 0.3	0.9 ± 0.1
Benzo (18-crown-6)	1.0 ± 0.2	3.8 ± 0.2	58.9 ± 0.4	38.5 ± 0.5	24.5 ± 0.6
7	1.9 ± 0.3	6.5 ± 0.4	65.7 ± 0.3	41.3 ± 0.3	31.6 ± 0.8
8	1.8 ± 0.2	4.2 ± 0.5	58.1 ± 0.4	36.1 ± 0.4	25.2 ± 0.4
9	0.7 ± 0.1	1.4 ± 0.1	49.5 ± 0.5	27.6 ± 0.6	19.4 ± 0.2

^a Aqueous phase (5 mL), [MOH] = 10⁻¹ M, [picric acid] = 10⁻³ M; organic phase (CH₂Cl₂, 5 mL), [ligand] = 10⁻³ M.

^b Average of three independent runs.

behaviour of the host compounds. A potential explanation is that for the first generation crown ether-functionalized dendrimers, donor atoms in the dendritic branching are able to interact, controlling the binding strength with the alkali metal cation, while steric repulsion is effective in the second and third generation crown ether-functionalized dendrimers. A rationale for the nega-

tive *dendritic effect* is perhaps the steric hindrance of the crown ether cavity caused by the dendritic branches, as the large dendritic fragments of the third generation provide a hydrophobic barrier against permeation of the metal ions, thus hindering guest binding.

On the NMR time-scale, the complexes are kinetically stable and show characteristic spectroscopic changes with respect to the free host compound. ¹H NMR titrations in CD₃CN revealed the stoichiometry of host:guest binding as 1:1, with clear titration profiles for the macrocyclic, benzylic and aromatic resonances of the host compounds indicating saturation of the crown ether-functionalized dendrimer receptors on the addition of one equivalent of alkali metal cation (Supplementary data). Moreover, the stoichiometry of host:guest binding was found to be independent of the dendrimer generation. Also, the ¹H NMR titrations allowed us to determine whether the crown ether moiety and the dendritic wedges cooperate in the binding of alkali metal cations. Figure 2 shows the ¹H NMR spectra of the host compound 7 upon addition of K⁺ in CD₃CN.

As expected, the signals of the crown ether protons shifted to a lower field by complexation with K⁺ cations. A similar, although less marked effect was observed for the benzylic protons of the two first generation dendrons, indicating three-dimensional interaction with the metal cation due to the cooperative binding that involves both the crown ether and the electron donor-containing

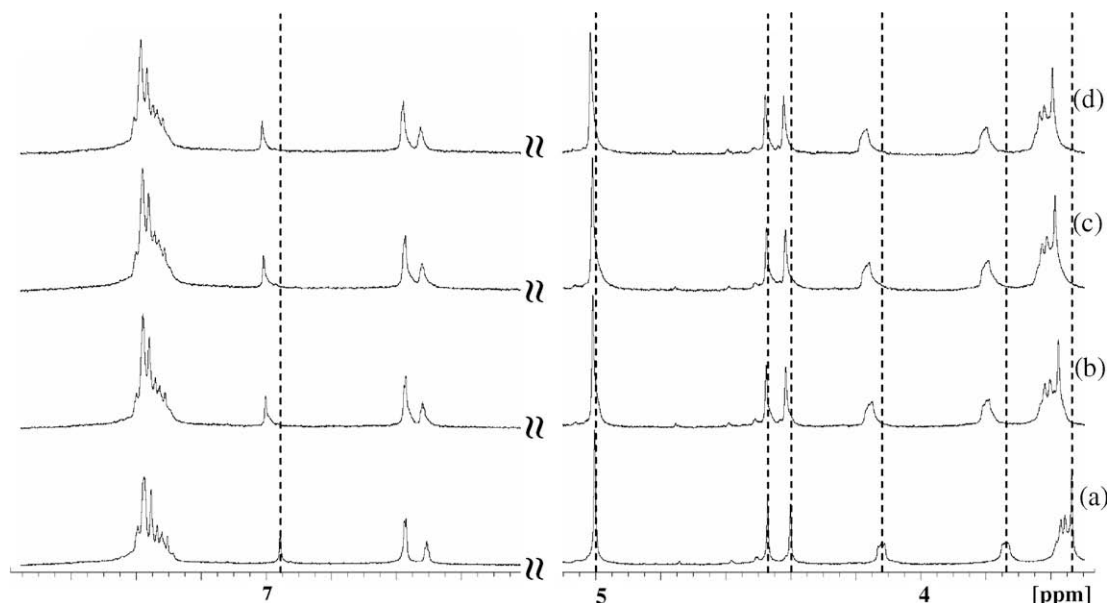


Figure 2. ^1H NMR spectra of free host **1** on binding with K^+ at 295 K in CD_3CN . (a) Free host **7**. (b) **7**+1 equiv of K^+ . (c) **7**+3 equiv of K^+ . (d) **7**+5 equiv of K^+ . The low field-shifted crown ether signals are labelled (dashed lines).

dendron moieties. On the contrary, the shifts of the benzylic protons for the second and third generation dendrimers were very small. From these results, it can be reasoned that for the first generation dendrimers, the cation is enveloped by donor groups present in both ring and poly(benzyl ether) dendrons, promoting complexation and extraction, while in the cases of second and third generation dendrimers, the dendritic wedges interfere with the binding behaviour.

In summary, the ability of a series of new crown ether-functionalized dendrimers to complex simple cationic guests has been investigated by liquid-liquid extraction and ^1H NMR titration experiments. It is shown that the Fréchet-type dendritic wedges of different generations, which are present in the studied compounds, display different extraction characteristics toward alkali metal cations. Positive and negative dendritic effects have been assigned to the complexation behaviour of the crown ether-functionalized dendrimers, which are dependent on the dendrimer generation. These findings may be helpful for the future design of crown ether and other macrocyclic ligand-based dendrimers.

Acknowledgements

This research was co-funded by the European Union in the framework of the program 'Pythagoras I' of the 'Operational Program for Education and Initial Vocational Training' of the 3rd Community Support Framework of the Hellenic Ministry of Education, funded 25% from national sources and 75% from the European Social Fund (ESF). We are sincerely thankful to Professor Edwin Weber (TU Freiberg, Germany) for his constructive comments during the preparation of the manuscript.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.08.053.

References and notes

- (a) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1039; (b) Baars, M. W. P. L.; Meijer, E. W. *Top. Curr. Chem.* **2000**, *210*, 131.
- (a) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495; (b) Pedersen, C. J. *Aldrichimica Acta* **1971**, *4*, 1.
- Pedersen, C. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1021.
- (a) *Host-Guest Complex Chemistry-Macrocycles*; Vögtle, F., Weber, E., Eds.; Springer: Berlin-Heidelberg, 1985; (b) *Synthesis of Macrocycles-The Design of Selective Complexing Agents*; Izatt, R. M., Christensen, J. J., Eds.; Progress in Macrocyclic Chemistry; Wiley: New York, 1987; Vol. 3, (c) *Crown Ethers and Analogs*; Patai, S., Rappaport, Z., Eds.; Wiley: Chichester, 1989.
- (a) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S. *Chem. Rev.* **1995**, *95*, 2529; (b) *Macrocyclic Polyethers*; Gokel, G. W., Korzeniowski, S. H., Eds.; Springer: Berlin, 1982.
- (a) Dietrich, B.; Lehn, J. M.; Sauvage, J. P. *Tetrahedron Lett.* **1969**, 2885; (b) Sutherland, I. O. *Heterocycles* **1984**, *21*, 235.
- Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1009.
- (a) *Supramolekulare Chemie*; Vögtle, F., Ed.; Teubner: Stuttgart, 1989; (b) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89; (c) Stoddart, J. F. *Ann. Rep. Prog. Chem.* **1988**, *85*, 353.
- (a) Vögtle, F.; Gestermann, S.; Hesse, R.; Schwierz, H.; Windisch, B. *Prog. Polym. Sci.* **2000**, *25*, 987; (b) Zeng, F.; Zimmermann, S. C. *Chem. Rev.* **1997**, *97*, 1681; (c) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74; (d) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689; (e) Smith, D. K.; Diederich, F. *Top. Curr. Chem.* **2000**, *97*, 183.
- (a) Dykes, G. M.; Smith, D. K. *Tetrahedron* **2003**, *59*, 3999; (b) Jiang, D.-L.; Aida, T. *Chem. Commun.* **1996**, 1523; (c) Collman, J. P.; Fu, L.; Zingg, A.; Diederich, F. *Chem. Commun.* **1997**, 193; (d) Smith, D. K.; Diederich, F. *Chem. Commun.* **1998**, 2501; (e) Bähr, A.; Felber, B.; Schneider, K.; Diederich, F. *Helv. Chim. Acta* **2000**, *83*, 1346; (f) Habicher, T.; Diederich, F.; Gramlich, V. *Helv. Chim. Acta* **1999**, *82*, 1066; (g) Kenda, B.; Diederich, F. *Angew. Chem., Int. Ed.* **1998**, *110*, 3357; (h) Newkome, G. R.; Godínez, L. A.; Moorefield, C. N. *Chem. Commun.* **1998**, 1821.
- (a) Chow, H.-F.; Leung, C.-F.; Wang, G.-X.; Yang, Y.-Y. *C. R. Chimie* **2003**, *6*, 735; (b) Lee, J.-J.; Ford, W. T.; Moore, J. A.; Li, Y. *Macromolecules* **1994**, *27*, 4632; (c) Breinbauer, R.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2000**, *39*, 3604; (d) Balzani, V.; Ceroni, P.; Gestermann, S.; Kauffmann, C.; Gorka, M.; Vögtle, F. *Chem. Commun.* **2000**, 853; (e) Newkome, G. R.; Güther, R.; Moorefield, C. N.; Cardullo, F.; Echegoyen, L.; Pérez-Cordero, E.; Luftmann, H. *Angew. Chem., Int. Ed.* **1995**, *34*, 2023; (f) Chow, H.-F.; Chan, I. Y.-K.; Chan, D. T. W.; Kwok, R. W. M. *Chem. Eur. J.* **1996**, *2*, 1085; (g) Jansen, J. F. G. A.; Peerlings, H. W. I.; de Brabander-Van den Berg, E. M. M.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1206; (h) Koenig, S.; Müller, L.; Smith, D. K. *Chem. Eur. J.* **2001**, *7*, 979; (i) Skobridis, K.; Hüsken, D.; Nicklin, P.; Häner, R. *Arkivoc* **2005**, *6*, 459.
- Alivertis, D.; Theodorou, V.; Paraskevopoulos, G.; Skobridis, K. *Tetrahedron Lett.* **2007**, *48*, 4091.