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CALIXARENES WITH APPENDED HETEROCYCLIC MOIETIES

Abstract: In the paper selected examples of calixarenes with appended heterocyclic moieties are presented, pointing out their complexing properties.

Introduction

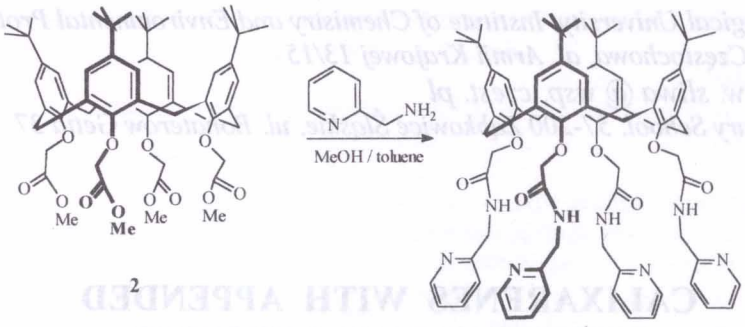
Calixarenes with appended heterocyclic moieties belong to family of calixarenes [1-6], compounds intensively studied, mainly as receptors of ionic and neutral species. Calixarenes with appended heterocyclic moieties should be distinguished from heterocalixarenes, i.e. heterocycle-based calixarenes having the cavity built by heterocyclic units [7,8].

Another class of compounds related to calixarenes are heteracalixarenes such as aza- [9-11], oxa- [12-14] and thiacalixarenes [15-17] in which bridges connecting phenol units contain N, O or S atoms, respectively. One should mention here also resorcarenes [18-20] built from resorcinol units, and cavitands [21-23] formed from resorcarenes by bridging resorcinol hydroxyl groups of neighboring aromatic rings.

Calixarenes with appended heterocyclic moieties are a topic of numerous works [24-26], in the present paper selected examples of these species will be described pointing out their complexing properties and application possibilities.

Examples of calixarenes with appended heterocyclic moieties

Compound **1** contains carbonyl groups and phenolic oxygen atoms able to complex hard cations, whereas four pyridine moieties can bind soft cations by the nitrogen atoms [27]. Compound **1** has been synthesized in the reaction of **2** with 2-(aminomethyl)pyridine [28].

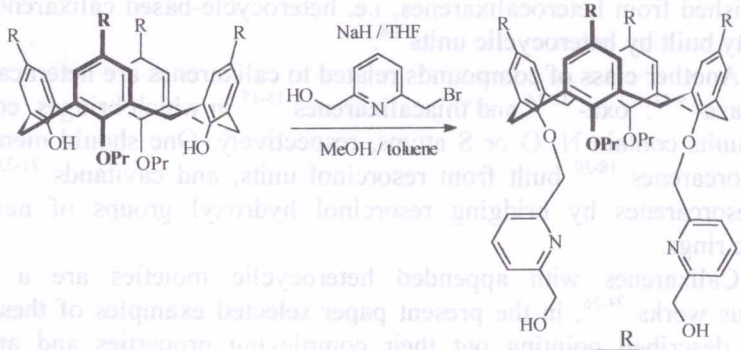


2 **1**

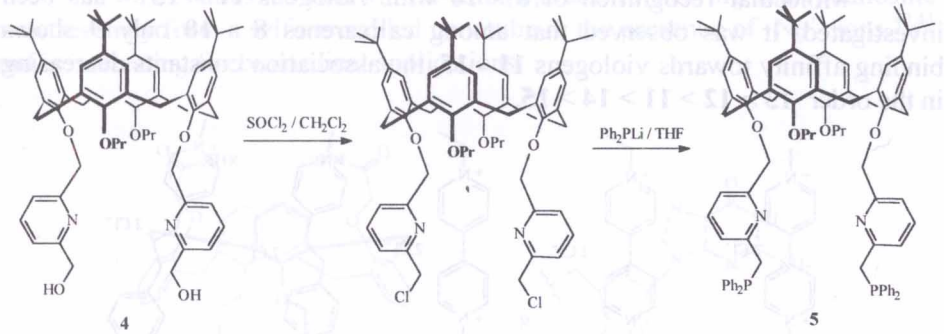
Complexing properties of **1** have been investigated. It was observed that **2** forms with Li^+, Na^+, Zn^{2+} and Mg^{2+} ions 1:1 complexes, with Cr^{2+} and Cu^{2+} - 1:2 complexes, and with Ni^{2+} and Co^{2+} - 2:1 complexes [28].

Calixarene derivatives may be used in the construction of ion-selective electrodes, sensitive among other to cesium [29,30], silver [31,32] thalium [33] and lead [34] ions. Ion-selective electrodes for Ag^+ containing calixarenes **3**,**4** and **5** have been prepared [35]. It was found that **3**,**4** and **5** show a good Ag^+ selectivity against alkali metal, alkaline-earth metal and lead ions and some transition metal ions (except for Hg^{2+}).

Calixarenes **3**,**4** and **5** have been synthesized as shown below [35]:

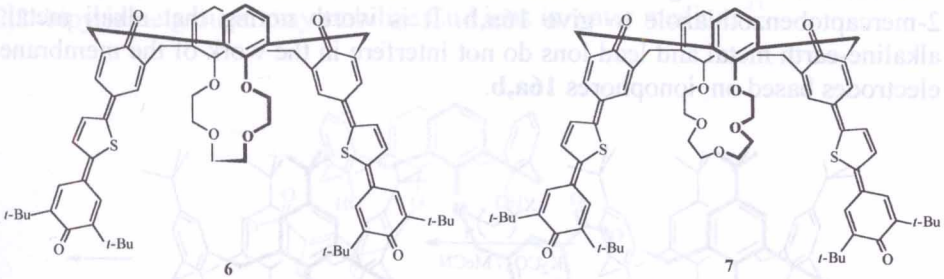


R	
3	H
4	*t*-Bu



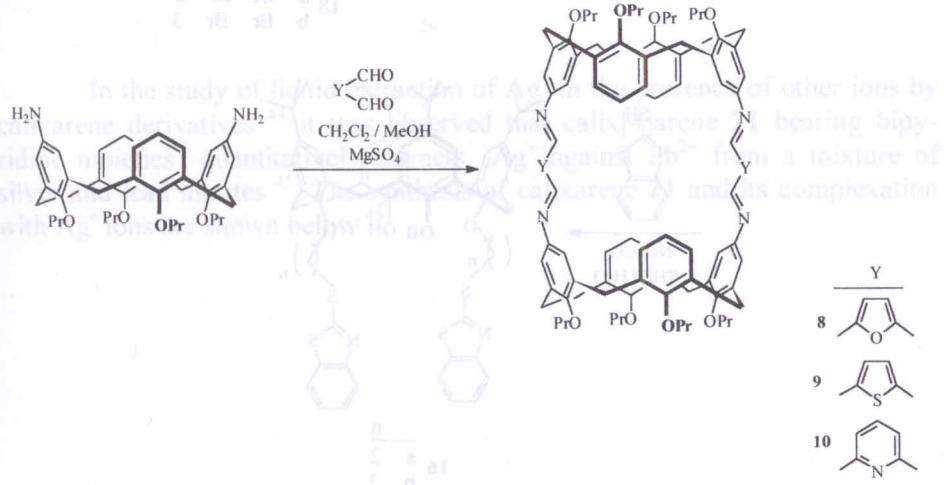
4 5

Calix[4]arenecrowns **6** and **7** bearing thienylene analog of *para*-terphenoquinone as chromophore have been synthesized [36]. It was observed that they undergo a significant color change upon complexation of Na^+ and K^+ ions.

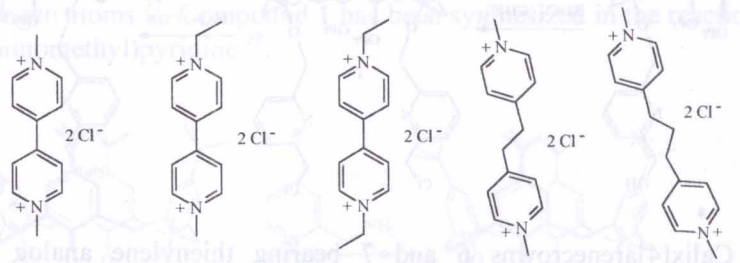


6 7

Nanometer-sized *bis*-calix[4]arenes **8** - **10** have been synthesized as follows [37].

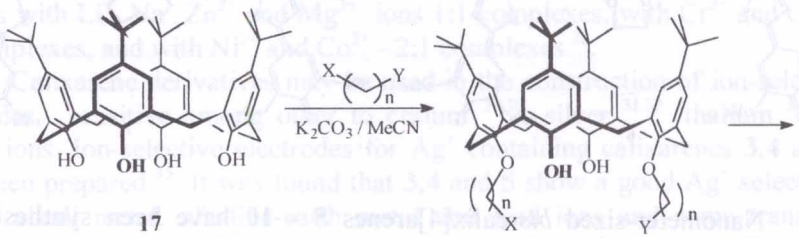


Molecular recognition of **8** - **10** with viologens **11** - **15** [38] has been investigated. It was observed that among calixarenes **8** - **10** only **9** shows binding affinity towards viologens **11** - **15**, the association constants decreasing in the order **13** > **12** > **11** > **14** > **15**.



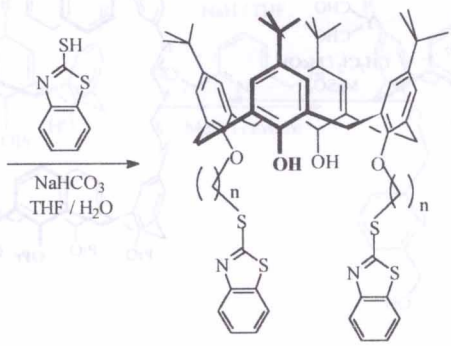
11 **12** **13** **14** **15**

Modified calixarenes **16a,b** are good ionophores for silver ion-selective electrodes [39]. Their synthesis begins with the reaction of calixarene **17** with dihaloalkanes leading to derivatives **18a,b**, which were treated with 2-mercaptobenzothiazole to give **16a,b**. It is worth noting that alkali metal, alkaline-earth metal and lead ions do not interfere in the work of the membrane electrodes based on ionophores **16a,b**.



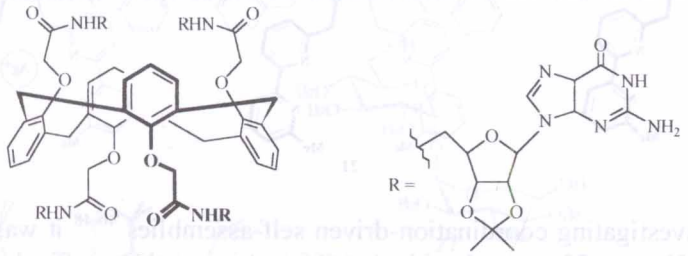
17

	X	Y	n
18 **a**	Cl	Br	2
b	Br	Br	3



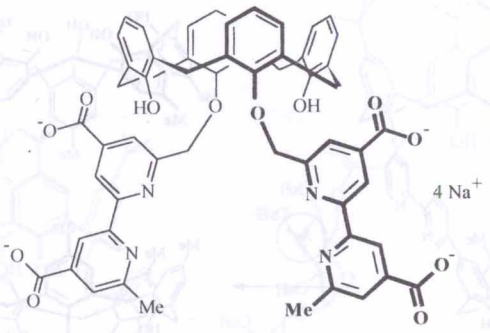
	n
16 **a**	2
b	3

It was established that 1,3-alt-calix[4]arene **19** bearing four guanosine moieties may form a self-assembled nanotube in the presence of Na^+ ions [40,41] and is interesting for biomedical applications.



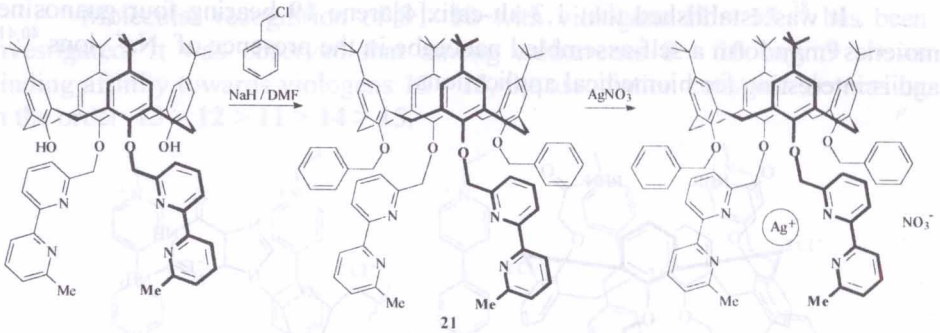
19

Calixarenes bearing bipyridine moieties show lipophilic [42] and hydrophilic [43] properties, for example the water-soluble calix[4]arene **20** containing 2,2'-bipyridine groups may stabilize Cu^+ ions in water medium [43].



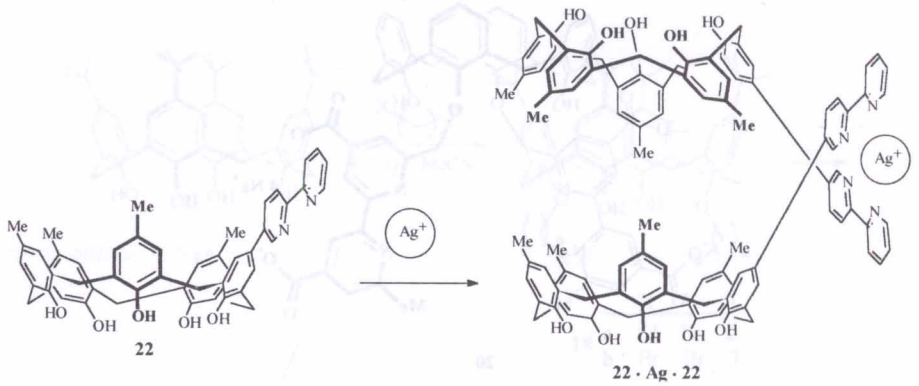
20

In the study of liquid extraction of Ag^+ in the presence of other ions by calixarene derivatives [44] it was observed that calix[4]arene **21** bearing bipyridine moieties quantitatively extracts Ag^+ against Pb^{2+} from a mixture of silver and lead nitrates [45]. The synthesis of calixarene **21** and its complexation with Ag^+ ions are shown below [45].



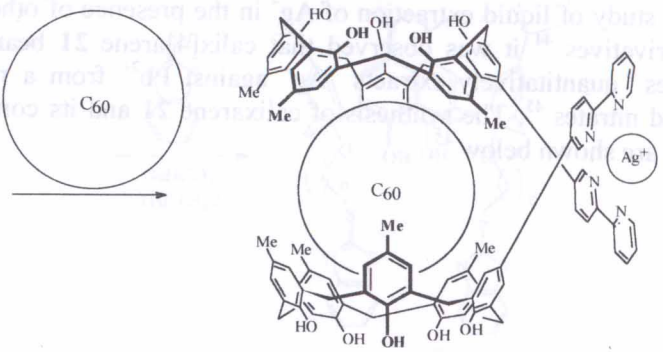
21

Investigating coordination-driven self-assemblies [46-48] it was found that the calix[5]arene **22** treated with AgOTf in nitromethane affords the ternary complex **22·Ag$^+$·22** which may serve as a receptor for C_{60} and C_{70} [49]. Silver cation complexation helds together two calix[5]arene moieties forming a cavity proper for the encapsulation of C_{60} or C_{70} molecules. Mixing of **22·Ag$^+$·22** with C_{60} leads to the formation of the complex **C_{60}@22·Ag·22**; similar complex was obtained with C_{70} [49].



22

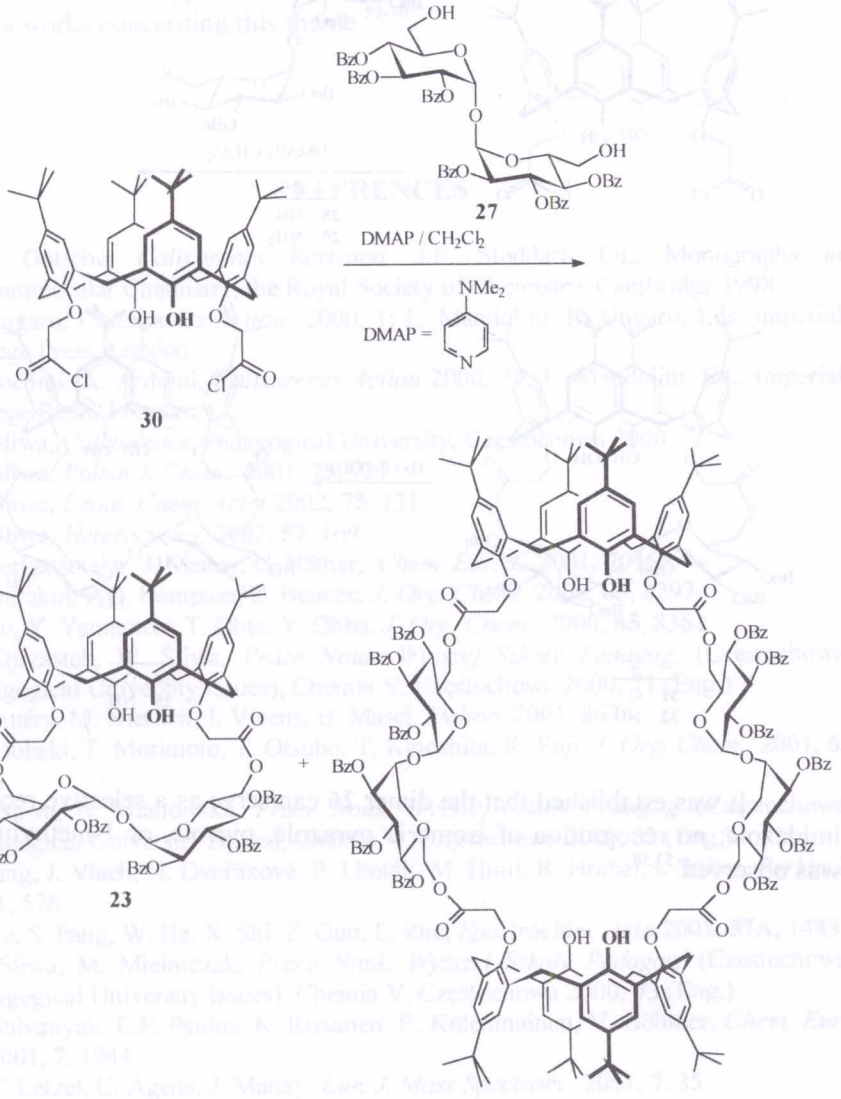
22 · Ag · 22



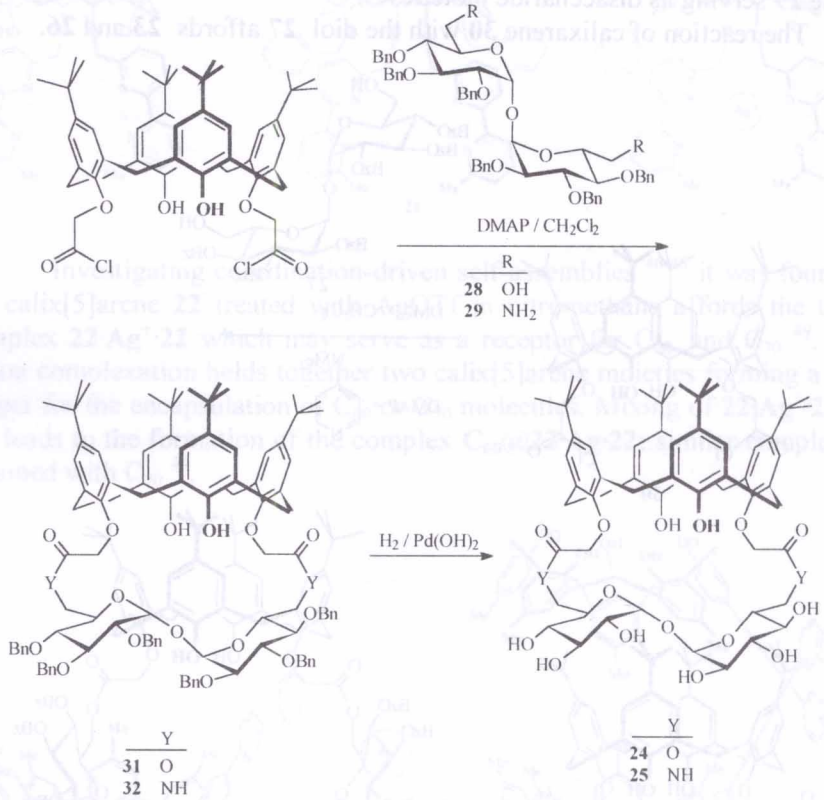
C60 @ 22 · Ag · 22

In the study of glycosylated calix[4]arenes [50-54] and resorcarenes [55,56], syntheses of bridged calixarenes **23**, **24** and **25** and of the dimer **26** have been made, the α,α-trehalose benzoylated and benzylated diols **27** and **28**, and the diamine **29** serving as disaccharide moieties [57].

The reaction of calixarene **30** with the diol **27** affords **23** and **26**.



The reaction of **30** with **28** and **29** leads to **31** and **32**, respectively, which after debenzylation *via* hydrogenolysis give **24** and **25**.



It was established that the dimer **26** can serve as a selective receptor for imidazole; no recognition of isomeric pyrazole, pyrrole, or 1-methylimidazole was observed [57,58]

Conclusion

Calixarenes with appended heterocyclic moieties are intensively studied due to their interesting properties, especially their recognition abilities promising in a variety of applications. The rapid development of investigations of calixarenes with appended heterocyclic moieties finds its reflection in numerous works concerning this theme [59-70].

REFERENCES

1. C.D. Gutsche, *Calixarenes Revisited,* J.F. Stoddart, Ed., Monographs in Supramolecular Chemistry, the Royal Society of Chemistry, Cambridge 1998
2. R. Ungaro, *Calixarenes Action* 2000, 1; L. Mandolini, R. Ungaro, Eds. Imperial College Press, London
3. A. Pochini, A. Arduini, *Calixarenes Action* 2000, 37; L. Mandolini, Ed., Imperial College Press, London
4. W. Śliwa, *Calixarenes,* Pedagogical University, Częstochowa 2000
5. W. Śliwa, *Polish J. Chem.* 2001, **75**, 921
6. W. Śliwa, *Croat. Chem. Acta,* 2002, **75**, 131
7. W. Sliwa, *Heterocycles,* 2002, **57**, 169
8. T. Gerkensmeier, J. Mattay, C. Näther, *Chem. Eur. J.* 2001, **7**, 465.
9. P. Chirakul, P.D. Hampton, Z. Bencze, *J. Org. Chem.* 2000, **65**, 8297
10. K. Ito, Y. Yamamori, T. Ohta, Y. Ohba, *J. Org. Chem.* 2000, **65**, 8361
11. L. Chrząstek, W. Śliwa, *Prace Nauk. Wyższej Szkoły Pedagog.* (Częstochowa Pedagogical University Issues), Chemia V, Częstochowa 2000, 71 (Eng.)
12. P, Thuéry, M. Nierlich, J. Vicens, B. Masci, *Dalton* 2001, 867
13. K. Tsubaki, T. Morimoto, T. Otsubo, T. Kinoshita, K. Fuji, *J. Org. Chem.* 2001, **6**, 4083
14. W. Śliwa, B. Mianowska, *Prace Nauk. Wyższej Szkoły Pedagog.* (Częstochowa Pedagogical University Issues), Chemia V, Częstochowa 2000, 83 (Eng.)
15. J. Lang, J. Vlach, H. Dvořáková, P. Lhoták, M. Himl, R. Hrabal, I. Stibor, *Perkin 2* 2001, 576
16. Z. Ye, S. Pang, W. He, X. Shi, Z. Guo, L. Zhu, *Spectrochim. Acta* 2001, **57A**, 1443
17. W. Śliwa, M. Mielniczak, *Prace Nauk. Wyższej Szkoły Pedagog.* (Częstochowa Pedagogical University Issues), Chemia V, Częstochowa 2000, 93 (Eng.)
18. A. Shivanyuk, E.F. Paulus, K. Rissanen, E. Kolehmainen, V. Böhmer, *Chem. Eur. J.* 2001, **7**, 1944
19. M.C. Letzel, C. Agena, J. Mattay, *Eur. J. Mass Spectrom.* 2001, **7**, 35
20. G. Arnott, P.C.B. Page, H. Heaney, R. Hunter, E.P. Sampler, *Synlett* 2001, 412
21. J.L. Irwin, M.S. Sherburn, *Org. Lett.* 2001, **3**, 225

22. K. Paek, H. Ihm, S. Yun, H.C. Lee, K.-T. No, *J. Org. Chem.* 2001, **66**, 5736
23. U. Lücking, J. Chen, D.M. Rudkevich, J. Rebek, Jr., *J. Am. Chem. Soc.* 2001, **123**, 9929
24. W. Śliwa, *Heterocycles* 2001, **55**, 181
25. M. Bochenska, R. Banach, A. Zielinska, V.C. Kravtsov, *J. Inclusion Phenom. Macrocyclic Chem.* 2001, **39**, 219
26. O.D. Mitkin, Y. Wan, A.N. Kurchan, A.G. Kutateladze, *Synthesis* 2001, 1133
27. A.F. Danil de Namor, *Coord. Chem. Rev.* 1999, **190**, 283
28. A. Hamdi, R. Abidi, M.T. Ayadi, P. Thuéry, M. Nierlich, Z. Asfari, J. Vicens, *Tetrahedron Lett.* 2001, **42**, 3595
29. J.S. Kim, A. Ohk, R. Ueki, T. Ishizuka, T. Shimotashiro, S. Maeda, *Talanta* 1999, **48**, 705
30. C. Péres-Jiméne, L. Escriche, J. Casabó, *Anal. Chim. Acta* 1998, **371**, 155
31. L. Chen, X. Zeng, X. He, Z.-Z. Zhang, *Fresenius J. Anal. Chem.*2000, **367**, 535
32. X. Zeng, L. Weng, L. Chen, X. Leng, Z.-Z. Zhang, X. He, *Tetrahedron Lett.* 2000, **41**, 4917
33. K. Kimura, K. Tatsumi, M. Yokoyama, M. Ouchi, M. Mocerino, *Anal. Commun.* 1999, **36**, 229
34. F. Cadogan, P. Kane, M.A. McKervey, D. Diamond, *Anal. Chem.* 1999, **71**, 5544
35. X. Zeng, L. Weng, L. Chen, X. Leng, H. Ju, X. He, Z.-Z. Zhang, *Perkin 2* 2001, 545
36. K. Takahashi, A. Gunji, D. Guillaumont, F. Pichierri, S. Nakamura, *Angew. Chem. Int. Ed.* 2000, **39**, 2925
37. G.T. Hwang, B.H. Kim, *Tetrahedron Lett.* 2000, **41**, 5917
38. Z. Zhong, A. Ikeda, S. Shinkai, *J. Am. Chem. Soc.* 1999, **121**, 11906
39. X. Zeng, L. Weng, L. Chen, X. Leng, Z. Zhang, X. He, *Tetrahedron Lett.* 2000, **41**, 4917
40. V. Sidorov, F.W. Kotch, M. El-Kouedi, J.T. Davis, *Chem. Commun.* 2000, 2369
41. S.L. Forman, J.C. Fettinger, S. Pieraccini, G. Gottarelli, J.T. Davis, *J. Am.Chem. Soc.*2000, **122**, 4060
42. J.-B. Regnouf-de-Vains, R. Lamartine, B. Fenet, *Helv. Chim. Acta* 1998, **81**, 661
43. N. Psychogios, J.-B. Regnouf-de-Vains, *Tetrahedron Lett.* 2001, **42**, 2799
44. A.T. Yordanov, B.R. Whittlesey, D.M. Rounhill, *Inorg. Chem.* 1998, **37**, 3526
45. J.-B. Regnouf-de-Vains, J.-O. Dalbavie, R. Lamartine, B. Fenet, *Tetrahedron Lett.* 2001, **42**, 2681
46. S. Leininger, B. Olenyuk, P.J. Stang, *Chem. Rev.* 2000, **100**, 853
47. D.L. Caulder, K.N. Raymond, *Acc. Chem. Res.* 1999, **32**, 975
48. M. Fujita, *Chem. Soc. Rev.* 1998, **27**, 417
49. T. Haino, H. Araki, Y. Yamanaka, Y. Fukazawa, *Tetrahedron Lett.* 2001, **42**, 3203
50. F.G. Calvo-Flores, J. Isac-Garcia, F. Hernández-Mateo, F. Pérez-Balderas, J.A. Calvo-Asin, E. Sanchéz-Vaquero, F. Santoyo-González, *Org. Lett.* 2000, **2**, 2499
51. J. Budka, M. Tkadlecová, P. Lhoták, I. Stibor, *Tetrahedron* 2000, **56**, 1883
52. C. Saitz-Barria, A. Torres-Pinedo, F. Santoyo-González, *Synlett* 1999, 1891
53. R. Roy, J.M. Kim, *Angew. Chem. Int. Ed.* 1999, **38**, 369

54. C. Félix, H. Parrot-Lopez, V. Kalchenko, A.W. Coleman, *Tetrahedron Lett.* 1998, **39**, 9171
55. O. Hayashida, K. Nishiyama, Y. Matsuda, Y. Aoyama, *Tetrahedron Lett.* 1999, **40**, 3407
56. O. Hayashida, C. Shimizu, T. Fujimoto, Y. Aoyama, *Chem. Lett.* 1998, 13
57. A. Dondoni, X. Hu, A. Marra, H.D. Banks, *Tetrahedron Lett.* 2001, **42**, 3295
58. K. Araki, H. Hayashida, *Chem. Lett.* 2000, 20
59. T. Gu, C. Bourgogne, J.-F. Nierengarten, *Tetrahedron Lett.* 2001, **42**, 7249
60. M. Giannetto, G. Mori, A. Notti, S. Pappalardo, M.F. Parisi, *Chem. Eur. J.* 2001, **7**, 3354
61. C.-M. Jin, G.-Y. Lu, Z.-S. Wang, X.-Z. You, Z.-H. Wang, W. Gong, H.-M. Wu, *Synthesis* 2001, 1023
62. Y. Liu, Y. Chen, L. Li, G. Huang, C.-C. You, H.-Y. Zhang, T. Wada, Y. Inoue, *J. Org. Chem.* 2001, **66**, 7209
63. F. Oueslati, I. Dumazet-Bonnamour, R. Lamartine, *Tetrahedron Lett.* 2001, **42**, 8177
64. X. Zeng, L. Weng, Z.-Z. Zhang, *Chem. Lett.* 2001, 550
65. S.E. Matthews, P. Parzuchowski, A. Garcia-Carrera, C. Grüttner, J.-F. Dozol, V. Böhmer, *Chem. Commun.* 2001, 417
66. O. Hayashida, A. Matsuo, Y. Aoyama, *Chem. Lett.* 2001, 272
67. Q. Ma, H. Ma, Z. Wang, M. Su, H. Xiao, S. Liang, *Chem. Lett.* 2001, 100
68. C.N. Baki, E.U. Akkaya, *J. Org. Chem.* 2001, **66**, 1512
69. J.B. Cooper, M.G.B. Drew, P.D. Beer, *Dalton* 2001, 392
70. Z. Zhong, A. Ikeda, M. Ayabe, S. Shinkai, S. Sakamoto, K. Yamaguchi, *J. Org. Chem.* 2001, **66**, 1002

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Kaliksareny o dołączonych układach heterocyklicznych

Streszczenie: W artykule przedstawiono wybrane przykłady kaliksarenów o dołączonych układach heterocyklicznych, szczególną uwagę zwracając na ich właściwości kompleksotwórcze.