ORIGINAL ARTICLE

# Molecular clips based on diphenylglycoluril and benzocrown ethers: promising complexing agents for the alkali metal cations

Leonid S. Kikot' · Alexander Yu. Lyapunov · Catherine Yu. Kulygina · Tatiana Yu. Bogaschenko · Roman I. Zubatyuk · Oleg V. Shishkin · Tatiana I. Kirichenko

Received: 30 May 2013/Accepted: 30 July 2013 © Springer Science+Business Media Dordrecht 2013

Abstract The interaction of new molecular clips containing diphenylglycoluril and benzocrown ethers moieties with alkali metals ions was studied. Stability constants were determined by spectrophotometric titrations with chloride salts in methanol. Complex stability and cation binding selectivity were shown to be dependent on the size of the crown ether moiety. The "sandwich-type" 1:1 (clip to cation) complexes and the "classical" 1:2 complexes were found. Their ratio varies depending on the molecular clips nature and on the cation type. It was found an unexpected selectivity of the molecular clip with benzo-15crown-5 moieties toward  $K^+$  and  $Rb^+$  cations. The molecular structure of the clip complex with benzo-15crown-5 fragments and sodium picrate was determined by X-ray crystallography. The crystal structure and solutionstate structure were proven to be similar.

**Electronic supplementary material** The online version of this article (doi:10.1007/s10847-013-0357-3) contains supplementary material, which is available to authorized users.

L. S. Kikot' · A. Yu. Lyapunov · C. Yu. Kulygina · T. Yu. Bogaschenko · T. I. Kirichenko (🖾) Department of Fine Organic Synthesis, A.V. Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine, Lustdorfskaya Doroga 86, Odessa 65080, Ukraine e-mail: ti-kirichenko@rambler.ru

R. I. Zubatyuk · O. V. Shishkin

Department of X-ray Diffraction Studies and Quantum Chemistry, SSI "Institute for Single Crystals", National Academy of Sciences of Ukraine, Lenina Ave. 60, Kharkiv 61001, Ukraine

O. V. Shishkin

Department of Inorganic Chemistry, V. N. Karazin Kharkiv National University, Svobody Sq. 4, Kharkiv 61077, Ukraine **Keywords** Molecular clip · Crown ether · Diphenylglycoluril · Host–guest complexes · Crystal structure · Alkali metals

### Introduction

The design and synthesis of receptors capable of selective binding to metal cations is a relevant and important task in host-guest chemistry [1-3]. The basis of these receptors, as a rule, is the central ionophore core binding substrate both strongly and selectively [4, 5]. The introduction of chromophores or fluorophores into molecular framework can create highly sensitive sensors for analyte measurement in vivo [6]. The incorporation of such sensors into membranes can lead to ion-selective electrodes for in vitro research [7, 8]. Thus, the receptors can be included into polymers through the introduction of reactive groups, furthermore, they can be immobilized on the surfaces of substrates suitable for the selective separation of mixtures [9–11]. Many scientists are interested in searching for receptors that can strongly and selectively bind alkali metal cations. In particular, ionophores for Na<sup>+</sup> and K<sup>+</sup>, which play a crucial role in maintaining the cell homeostasis, are widely used in creation of probes that can operate directly in the living organisms [12, 13]. Complexones which bind <sup>137</sup>Cs strongly and selectively in acidic media can be used at the reprocessing the spent nuclear fuel and radioactive waste [14–17]. Studies in this field are still relevant despite the huge number of the obtained complexones. Crown ethers (CE) and their derivatives dominate over numerous recently reported synthetic receptors capable to bind cations of alkali and/or alkaline earth metals [18, 19]. Last years, biscrown ethers with two CE fragments bound by various linkers, draw increasing interest of researchers

[19]. Earlier studies of some bis(crown ether) derivatives have established that they generally exhibit larger stability constants and higher metal cation binding selectivity than corresponding mono-crown ethers [19–22]. The use of a rigid molecular fragment as a linker allows obtaining preorganized receptor-molecular clip with pre-determined properties (spatial arrangement of the CE moieties, the distance from each other, etc.) [23, 24]. Glycoluril and its derivatives are characterized by great popularity among the large number of molecular fragments that can act as a rigid linker [25–27]. A large number of different synthetic receptors were obtained on the glycoluril basis, for instance: cucurbiturils [28, 29], "tennis ball" and "soft ball" [30, 31], molecular baskets and variety of molecular clips [32–35]. The latter represent receptors comprising a rigid diphenylglycoluril framework bound up with two aromatic walls through four bridging methylene groups. Forming pseudocavity, molecular clips can hold various substrates inside due to a set of non-covalent interactions [36-41].

It has previously been qualitatively shown by us that molecular clips based on the diphenylglycoluril and benzocrown ethers are capable to form host–guest inclusion complexes with alkali metal cations of different stoichiometry, and also to extract them from the aqueous phase to the organic one [42].

Here we report the study of the influence of alkali metal cation size on the interactions with molecular clips containing different crown ethers moieties. There are presented the stability constants, that quantitatively reflect the complexing properties of molecular clips 1-5 with alkali metal chlorides in methanol, and the structure of complex 2 with sodium picrate in the solid state.

#### Experimental

#### General

UV–Vis absorption spectra (220–800 nm) were obtained using a Carl Zeiss Specord M40 spectrophotometer in a 10 mm path length quartz cuvette. Molecular clips **1–5** were prepared as described [42–44]. All of alkali metal chlorides were of analytical grade.

# UV-Vis titration experiments

A solution of molecular clip **1–5** (concentration about  $7 \times 10^{-5}$  M) in methanol was treated with increasing amounts of alkali metal chloride solution (concentration about  $2 \times 10^{-3}$  M) containing proper molecular clip of the same concentration at 20 °C. The host concentration was

maintained constant and the molar ratio of guest increased with respect to the host over the range 0.2:1-20:1 during the titration. The absorbance measurements were carried out at four wavelengths, at which spectral changes were the most notable (220–290 nm) simultaneously, and sets of the obtained experimental values (4 × 30 points) were used for joint computer processing. The data were processed with the nonlinear least squares fitting SIRKO [45] software (see Supplementary data).

X-ray crystallographic investigations

Crystals suitable for X-ray diffraction were grown by crystallization of equimolar mixture of 2 and sodium picrate from EtOH-Me<sub>2</sub>CO-H<sub>2</sub>O mixture (2:2:1 v/v). X-ray diffraction study of  $\mathbf{2} \subset \text{Na}$  picrate complex (C<sub>114</sub>H<sub>124</sub>N<sub>17</sub>O<sub>50</sub>Na<sub>3</sub>, Mr = 2.601.27) was performed on an Xcalibur 3 diffractometer at 100 K. Crystal data: a = 17.7944(4), b =35.8060(6), c = 20.8412(4) Å,  $\beta = 108.956(2)^{\circ}$ , V =12,558.7(4) Å<sup>3</sup>, monoclinic, space group P2<sub>1</sub>/n, Z = 4,  $\mu$ (Mo K<sub> $\alpha$ </sub>) = 0.118 mm<sup>-1</sup>, d<sub>calc</sub> = 1.376 g mm<sup>-3</sup>, 72,516 reflections measured up to  $2\theta_{max} = 56.96^{\circ}$ , 28262 unique  $(R_{int} = 0.054)$  which were used in all calculations. Structure was solved by direct methods and refined in anisotropic approximation for all non-hydrogen atoms using SHELX-97 software [46]. Hydrogen atoms refined in riding model with  $U_{iso} = nU_{eq}$  of the carrier atom (n = 1.2 for C-H and n = 1.5 for O–H). Heavily disordered unidentified solvent was found in the crystal structure in the cavities of 345.1  $\text{\AA}^3$ (4 per unit cell) with integrated number of electrons of 9.5. The contribution from disordered solvent was removed by BYPASS procedure [47], implemented in Olex-2 software [48]. Refinement converged to  $wR_2 = 0.140$  (all data),  $R_1 = 0.056$  (for 16,228 reflections with  $I > 2\sigma(I)$ ), S = 0.98. Crystallographic data (excluding structure factors) for the structure in given paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 910558. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

# **Results and discussion**

# Synthesis

Synthesis of molecular clips was carried out through the interaction of bisether **6** with the corresponding benzocrown ethers **7–11** in PPA according to the method described previously by us (Scheme 1) [42-44]. Scheme 1 Synthesis of molecular clips 1–5



Complexation studies

The stoichiometry and stability constants of the complexes formed by molecular clips 1-5 and alkali metal chlorides were determined by spectrophotometric titration using mole ratio method in methanol at 20 °C [49, 50]. The experimental data were processed with a non-linear least squares method using the SIRKO software [45]. Analysis of the experimental data revealed the presence of two types of complexes, namely the complexes with ligand to metal (L/M) composition equal to 1:1 and 1:2. The stability constants were determined considering the following equilibria:

$$L + M \rightleftharpoons LM \qquad K_1 = \frac{[LM]}{[L][M]}$$
$$LM + M \rightleftharpoons LM_2 \qquad K_2 = \frac{[LM_2]}{[LM][M]}$$

where  $K_1$  and  $K_2$  correspond to the stability constants of the 1:1 and 1:2 complexes; [L], [M], [LM], [LM<sub>2</sub>] denote the equilibrium concentration of the metal cations, molecular clip, and their 1:1 and 1:2 complexes, respectively.

As can be seen from the data (Table 1; Fig. 1), the molecular clip **1** shows very poor selectivity for the investigated ions. This is probably caused by a small number of donor oxygen atoms of molecular clip pseudocavity, and, as a result, stability of complexes changes slightly depending on the cavity/cation size ratio. The constants values for **1** are also small and decrease with the increasing the cation size. Furthermore, low selectivities are observed for molecular clips **4** 

and **5** despite the high constants of complexation. Noteworthy, in the **3–5**, and to a lesser degree in **2**, CE fragments can act as independent units that results in the 1:2 complex formation in essential quantities. The stability of these complexes is, as a rule, several orders of magnitude lower compared to similar 1:1 complexes, the correlation between macrocycle/cation size is not observed. The most interesting results have been obtained for the molecular clips **2** and **3**. Thus, the stability of the complexes **2** with K<sup>+</sup> and Rb<sup>+</sup> is maximum in molecular clips obtained by us, and exceeds that of the complexes with Na<sup>+</sup> and Cs<sup>+</sup> by ~2.5 orders of magnitude. Stability of the complexes **3** increases with increasing of the cation size and reaches a maximum for Cs<sup>+</sup>.

These results are in good agreement with the data obtained at the qualitative study of the complexation properties of molecular clips under mass spectrometric and picrate extraction experiments conditions [42]. Such high values of the stability constants for the **2** and **3** indicate the formation of sandwich type complexes when the metal cation is located in pseudocavity (Fig. 2a) formed by two CE fragments of molecular clip. As a result, the metal cation interacts simultaneously with a greater number of donor atoms that leads to a substantial increase of the stability constants compared to the analogous CE [51–54].

Selectivity of the obtained molecular clips concerning alkali metals cations differs also from that observed for CE's [51, 52]. For example, molecular clip **2** through two ideal spatially proximate fragments of benzo-15-crown-5 forms an extremely stable complex with Rb<sup>+</sup>, what is not typical for benzo-15-crown-5 [54]. A possible explanation

Table 1 Stability constants of the complexes of molecular clips 1–5 with alkali metal cations in MeOH

Cation	Compound									
	1		2		3		4		5	
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
Na <sup>+</sup>	$3.27\pm0.04$	_	$4.13\pm0.04$	$2.90\pm0.02$	$4.51\pm0.05$	$2.09\pm0.07$	N/D <sup>a</sup>	N/D <sup>a</sup>	N/D <sup>a</sup>	N/D <sup>a</sup>
$K^+$	$3.28\pm0.03$	-	$6.25\pm0.07$	_	$4.96\pm0.04$	$1.64\pm0.06$	$4.44\pm0.06$	$1.20\pm0.05$	$4.64\pm0.02$	$2.89\pm0.01$
$Rb^+$	$2.78\pm0.06$	_	$6.34\pm0.08$	_	$5.23\pm0.01$	$3.32\pm0.06$	$4.51\pm0.10$	$1.28\pm0.09$	$4.05\pm0.05$	$1.53\pm0.06$
$Cs^+$	$2.59\pm0.04$	-	$3.74\pm0.02$	-	$5.92\pm0.13$	$1.48\pm0.07$	$4.43\pm0.04$	$3.63\pm0.05$	$4.93\pm0.08$	$2.28\pm0.03$

<sup>a</sup> The changes in spectrum were too small and it was impossible to calculate the binding constant



Fig. 1 The log K values for interactions of molecular clips 1–5 with alkali metal cations

for the selectivity of 2 is that the binding of the larger cation (e.g. Cs<sup>+</sup>) causes substantial rearrangement of pseudocavity and somewhat of the diphenylglycoluril frame (angle between the phenyl rings).

This should lead to the tension of 1,3-benzodiazepine fragment in glycoluril frame, making the process less favorable (Fig. 2b). Higher conformational flexibility of polyether chains in 4 and 5 allows "host" to realize conformational changes with less energetic losses, what leads to a notable selectivity decrease, while the high values of the stability constants remain almost unchanged. Molecular clip 3 is in intermediate position by both the efficiency and selectivity of complexation.

Stability of the 1:2 complexes of described clips is significantly lower than that of 1:1 ones. Ratio  $4K_2/K_1 < 1$  [55] clearly indicates anticooperative effect due to electrostatic repulsion of the two cations (Fig. 2c) located nearby. Complexes of such stoichiometry are not formed in the case of molecular clip 1, and in the case of 2 they are registered for Na<sup>+</sup> only. In the solid state, the molecular clip 2 forms the 3:2 complex with sodium picrate.

#### Molecular and crystal structure

The X-ray diffraction study of molecular clip 2 complex (Fig. 3) has demonstrated its dimeric character. The CE fragment of one clip is inserted into cavity formed by the CE fragments of the other molecule. In the complex each Na<sup>+</sup> cation is located within its own CE cavity and coordinated by all six oxygen atoms of the CE macrocycle, as well as, by the oxygen atoms of water molecules and picrate anions. Both outer CE rings contain the Na<sup>+</sup> cations coordinated additionally by the oxygen atoms of picrate anion, and one of the Na<sup>+</sup> cations is coordinated also by the water molecule located at the same side as the anion. As a result, cations are shifted by 1.09-1.19 Å from the mean plane of etheric oxygen atoms. One of the inner CE rings contains the Na<sup>+</sup> cation in the ring center coordinated in both axial directions by water molecules, and the other inner CE ring is empty and hydrogen bonded with two water molecules in axial directions. Similar coordination pattern has been found in the crystal of 15-crown-5 with lithium chlorochromate complex [56]. Due to symmetric environment, the inner CE ring adopts an almost perfect boat conformation and cation is located almost within the mean plane of the CE oxygen atoms (deviation is 0.07 Å). Two inner CE rings are nearly parallel (the angle between mean planes is  $4.5^{\circ}$ ). The outer rings are inclined related to inner one by 43-46°. Two clip molecules in the complex have similar conformation and are oriented approximately centrosymmetrically with respect to each other. Clip molecules are linked with each other by the O-H-O hydrogen bonds with water molecules. Thus, the complex could be considered as hydrogen-bonded clipped dimer of two 1:1 and 1:2 complexes.

X-ray diffraction data are in good agreement with the fact that whereas  $K_1$  for Na<sup>+</sup> is relatively small,  $K_2$  value is quite high. This confirms that there is equilibrium in the solution between the particles of the both 1:1 and 1:2 stoichiometry observed also in the solid state.

Fig. 2 Schematic representation of cooperative (a), anticooperative (c), effects for complexes with different stoichiometry and possible structural changes in host molecule (b)



**Fig. 3** Molecular structure of molecular clip **2** complex with sodium picrate 2:3 according to X-ray diffraction data. Displacement ellipsoids are shown at 50 % probability level



# Conclusions

In summary, molecular clips obtained by us show selectivity to certain alkali metal ions. Clips 4 and 5 form quite stable complexes with  $K^+$ ,  $Rb^+$  and  $Cs^+$  cations, whereas the stability of their complexes with  $Na^+$  is much lower. This can be used to separate  $K^+$ ,  $Rb^+$  and  $Cs^+$  cations from the excess of  $Na^+$ . The obtained clips can be prospective as a base for the design of new chemosensors through the "indicator groups" introduced in the existing frame for in vivo measuring, as well as, for the creation of ionselective electrodes for in vitro measuring. These clips can also be used in the design of sorbents and new functional materials for the selective extraction of ions from the mixture through the introduction of groups promoting immobilization of molecules on different carriers.

#### References

- 1. Atwood, J.L., Steed, J.W.: Encyclopedia of supramolecular chemistry. Marcel Dekker, Inc., New York (2004)
- Diederich, F., Stang, P., Tykwinski, R.R.: Modern supramolecular chemistry: strategies for macrocycle synthesis. Wiley, Weinheim (2008)
- Albelda, M.T., Frías, J.C., García-España, E., Schneider, H.-J.: Supramolecular complexation for environmental control. Chem. Soc. Rev. 41, 3859–3877 (2012)
- Anslyn, E.V.: Supramolecular analytical chemistry. J. Org. Chem. 72, 687–699 (2007)

- Bryant, J.A., Helgeson, R.C., Knobler, C.B., DeGrandpre, M.P., Cram, D.J.: Host–guest complexation. 53. Functional groups preorganized in hemispherands for binding alkali metal and ammonium cations. J. Org. Chem. 55, 4622–4634 (1990)
- Qian, F., Zhang, C., Zhang, Y., He, W., Gao, X., Hu, P., Guo, Z.: Visible light excitable Zn<sup>2+</sup> fluorescent sensor derived from an intramolecular charge transfer fluorophore and its in vitro and in vivo application. J. Am. Chem. Soc. **131**, 1460–1468 (2009)
- Bobacka, J., Ivaska, A., Lewenstam, A.: Potentiometric ion sensors. Chem. Rev. 108, 329–351 (2008)
- Wang, S.-H., Chou, T.-C.: Immobilized ionophore calcium ion sensor modified by montmorillonite. Electroanalysis 12, 468–470 (2000)
- Yost Jr, T.L., Fagan, B.C., Allain, L.R., Barnes, C.E., Dai, S., Sepaniak, M.J., Xue, Z.: Crown ether-doped sol-gel materials for strontium(II) separation. Anal. Chem. **72**, 5516–5519 (2000)
- Popova, N.N., Zhilov, V.I., Demin, S.V., Tsivadze, A.Yu., Yakshin, V.V., Vilkova, O.M.: Americium(III) sorption from multicomponent solutions by macrocyclic polyester-based sorbents. Russ. J. Inorg. Chem. 56, 1128–1132 (2011)
- Alexandratos, S.D., Stine, C.L.: Synthesis of ion-selective polymersupported crown ethers: a review. React. Funct. Polym. 60, 3–16 (2004)
- Gunnlaugsson, T., Nieuwenhuyzen, M., Richard, L., Thoss, V.: A novel optically based chemosensor for the detection of blood Na<sup>+</sup>. Tetrahedron Lett. 42, 4725–4728 (2001)
- Nandhikonda, P., Begaye, M.P., Heagy, M.D.: Highly watersoluble, OFF–ON, dual fluorescent probes for sodium and potassium ions. Tetrahedron Lett. 50, 2459–2461 (2009)
- Lee, S.H., Ko, S.W., Cho, E.J., Chun, J.C., Nam, K.C.: Phenylene bridged calix[6]arenes: cesium selective ionophores. Bull. Korean Chem. Soc. 22, 100–102 (2001)
- Zhang, A., Hu, Q., Chai, Z.: Synthesis of a novel macroporous silica-calix[4]arene-crown polymeric composite and its adsorption for alkali metals and alkaline-earth metals. Ind. Eng. Chem. Res. 49, 2047–2054 (2010)

- Ji, H.-F., Dabestani, R., Hettich, R.L., Brown, G.M.: Optical sensing of cesium using 1,3-alternate calix[4]-mono- and di(anthrylmethyl)aza-crown-6. Photochem. Photobiol. 70, 882–886 (1999)
- Zhang, A., Hu, Q.: Adsorption of cesium and some typical coexistent elements onto a modified macroporous silica-based supramolecular recognition material. Chem. Eng. J. 159, 58–66 (2010)
- Gokel, G.W., Leevy, W.M., Weber, M.E.: Crown ethers: sensors for ions and molecular scaffolds for materials and biological models. Chem. Rev. 104, 2723–2750 (2004)
- An, H., Bradshaw, J.S., Izatt, R.M., Yan, Z.: Bis- and oligo(benzocrown ether)s. Chem. Rev. 94, 939–991 (1994)
- Kimura, K., Yokota, G., Yokoyama, M., Uda, R.M.: Cation complexation and photochromism of copolymers carrying pendant crowned malachite green moiety. Macromolecules 34, 2262–2268 (2001)
- Liu, Y., Tong, L.H., Huang, Sh., Tian, B.Zh., Inoue, Y., Hakushi, T.: Complexation thermodynamics of bis(crown ether)s. 4. Calorimetric titration of intramolecular sandwich complexation of thallium and sodium ions with bis(15-crown-5)s and bis(12crown-4)s: enthalpy-entropy compensation. J. Phys. Chem. 94, 2666–2670 (1990)
- Inoue, Y., Hakushi, T., Liu, Y., Tong, L., Hu, J., Zhao, G., Huang, Sh., Tian, B.: Complexation thermodynamics of bis(crown ether)s. 2. Calorimetric titration of complexation of potassium ion with bis(benzocrown ether)s: enthalpy-entropy compensation. J. Phys. Chem. **92**, 2371–2374 (1988)
- Hardouin-Lerouge, M., Hudhomme, P., Sallé, M.: Molecular clips and tweezers hosting neutral guests. Chem. Soc. Rev. 40, 30–43 (2011)
- Leblond, J., Petitjean, A.: Molecular tweezers: concepts and applications. ChemPhysChem. 12, 1043–1051 (2011)
- Butler, A.R., Leitch, E.: Mechanistic studies in the chemistry of urea. Part 4. Reactions of urea, 1-methylurea, and 1,3-dimethylurea with benzil in acid solution. J. Chem. Soc., Perkin Trans. 2, 103–105 (1980)
- Creaven, B.S., Gallagher, J.F., McDonagh, J.P., McGinley, J., Murray, B.A., Whelan, G.S.: A new binding motif in molecular clips: 1-D polymeric self-inclusion in a phenol complex of a bis(methoxyphenyl)glycoluril. Tetrahedron 60, 137–143 (2004)
- Li, Y., Yin, G., Guo, H., Zhou, B., Wu, A.: One-pot synthesis of novel molecular clips and macrocyclic polyamines derived from bis(ethoxycarbonyl)glycoluril. Synthesis 17, 2897–2902 (2006)
- Lee, J.W., Samal, S., Selvapalam, N., Kim, H.-J., Kim, K.: Cucurbituril homologues and derivatives: new opportunities in supramolecular chemistry. Acc. Chem. Res. 36, 621–630 (2003)
- Kim, K., Selvapalam, N., Oh, D.H.: Cucurbiturils—a new family of host molecules. J. Incl. Phenom. Macrocycl. Chem. 50, 31–36 (2004)
- Conn, M.M., Rebek Jr, J.: Self-assembling capsules. Chem. Rev. 97, 1647–1668 (1997)
- Vriezema, D., Aragonès, M.C., Elemans, J.A.A.W., Cornelissen, J.J.L.M., Rowan, A.E., Nolte, R.J.M.: Self-assembled nanoreactors. Chem. Rev. 105, 1445–1490 (2005)
- Reek, J.N.H., Elemans, J.A.A.W., de Gelder, R., Beurskens, P.T., Rowan, A.E., Nolte, R.J.M.: Self-association and self-assembly of molecular clips in solution and in the solid state. Tetrahedron 59, 175–185 (2003)
- Escuder, B., Rowan, A.E., Feiters, M.C., Nolte, R.J.M.: Enantioselective binding of amino acids and amino alcohols by selfassembled chiral basket-shaped receptors. Tetrahedron 60, 291–300 (2004)
- Wang, Z.-G., Zhou, B.-H., Chen, Y.-F., Yin, G.-D., Li, Y.-T., Wu, A.-X., Isaacs, L.: Substituent effects control the self-association of molecular clips in the crystalline state. J. Org. Chem. 71, 4502–4508 (2006)
- Polavarapu, P., Melander, H., Langer, V., Gogoll, A., Grennberg, H.: Modulation and binding properties of extended glycoluril molecular clips. New J. Chem. 32, 643–651 (2008)
- 🖄 Springer

- Salonen, L.M., Ellermann, M., Diederich, F.: Aromatic rings in chemical and biological recognition: energetics and structures. Angew. Chem. Int. Ed. 50, 4808–4842 (2011)
- Meyer, E.A., Castellano, R.K., Diederich, F.: Interactions with aromatic rings in chemical and biological recognition. Angew. Chem. Int. Ed. 42, 1210–1250 (2003)
- Ghosh, S., Wu, A., Fettinger, J.C., Zavalij, P.Y., Isaacs, L.: Selfsorting molecular clips. J. Org. Chem. 73, 5915–5925 (2008)
- Nishio, M.: The CH/π hydrogen bond in chemistry. Conformation, supramolecules, optical resolution and interactions involving carbohydrates. Phys. Chem. Chem. Phys. 13, 13873–13900 (2011)
- Steiner, T.: The hydrogen bond in the solid state. Angew. Chem. Int. Ed. 41, 48–76 (2002)
- Blokzijl, W., Engberts, J.B.F.N.: Hydrophobic effects. Opinions and facts. Angew. Chem. Int. Ed. Engl. 32, 1545–1579 (1993)
- 42. Bogaschenko, T.Yu., Lyapunov, A.Yu., Kikot', L.S., Mazepa, A.V., Botoshansky, M.M., Fonari, M.S., Kirichenko, T.I.: Synthesis, crystal structure, and alkali metal picrate extraction capabilities of molecular clips based on diphenylglycoluril and benzocrown ethers. Tetrahedron 68, 4757–4764 (2012)
- Kikot', L.S., Lyapunov, A.Yu., Zubatyuk, R.I., Shishkin, O.V., Kirichenko, T.I.: Molecular clip based on diphenylglycoluril and catechol: promising building block of supramolecular structures. Synlett 23, 1897–1900 (2012)
- 44. Lyapunov, A.Yu., Pastushok, V.N., Kirichenko, T.I., Kulygina, C.Yu., Kikot', L.S., Bogaschenko, T.Yu., Luk'yanenko, N.G.: Synthesis and alkali metal picrate extraction capabilities of novel bis(benzocrown ethers) based on diphenylglycoluril. Macroheterocycles 3, 86–92 (2010)
- 45. Vetrogon, V.I., Lukyanenko, N.G., Schwing-Weill, M.-J., Arnaud-Neu, F.: A PC compatible computer program for the calculation of equilibrium constants by the simultaneous processing of different sets of experimental results. Talanta 41, 2105–2112 (1994)
- Sheldrick, G.M.: A short history of SHELX. Acta Crystallogr A. 64, 112–122 (2008)
- van der Sluis, P., Spek, A.L.: BYPASS: an effective method for the refinement of crystal structures containing disordered solvent regions. Acta Crystallogr A. 46, 194–201 (1990)
- Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Crystallogr. 42, 339–341 (2009)
- Beck, M., Nagypal, I.: Chemistry of complex equilibria. Academiai Kiado, Budapest (1989)
- Connors, K.A.: Binding constants: the measurement of molecular complex stability. Wiley, New York (1987)
- Izatt, R.M., Bradshaw, J.S., Nielsen, S.A., Lamb, J.D., Christensen, J.J., Sen, D.: Thermodynamic and kinetic data for cationmacrocycle interaction. Chem. Rev. 85, 271–339 (1985)
- 52. Izatt, R.M., Pawlak, K., Bradshaw, J.S., Bruening, R.L.: Thermodynamic and kinetic data for macrocycle interactions with cations and anions. Chem. Rev. **91**, 1721–2085 (1991)
- Izatt, R.M., Pawlak, K., Bradshaw, J.S., Bruening, R.L.: Thermodynamic and kinetic data for macrocycle interaction with cations, anions, and neutral molecules. Chem. Rev. 95, 2529–2586 (1995)
- Bartsch, R.A., Eley, M.D.: Syntheses of bis- and tetra-crowned clefts and studies of their selectivities in metal ion complexation. Tetrahedron 52, 8979–8988 (1996)
- Connors, K.A.: In: Atwood, J.L., Davies, J.E.D., MacNicol, D.D., Vögtle, F. (eds.) Comprehensive supramolecular chemistry 3, pp. 205–241. Pergamon, Oxford (1996)
- Shishkin, O.V., Zubatyuk, R.I., Zhovtyak, O.Yu., Kiriyak, A.V., Kotlyar, S.A., Kamalov, G.L.: Unexpected 3:2 stoichiometry and structure of 15-crown-5 complex with lithium chlorochromate. Struct. Chem. 20, 139–143 (2009)