Monatsh Chem (2010) 141:737–741
DOI 10.1007/s00706-010-0313-5

ORIGINAL PAPER

A combined extraction and DFT study on the complexation of H_3O^+ with a hexaarylbenzene-based receptor

Petr Toman · Emanuel Makrlík · Petr Vaňura ·
Václav Kašička · Rajendra Rathore

Received: 24 February 2010 / Accepted: 16 April 2010 / Published online: 12 May 2010

Abstract From extraction experiments in the two-phase water/nitrobenzene system and γ-activity measurements, the stability constant of a hexaarylbenzene-based receptor·H_3O^+ complex species dissolved in nitrobenzene saturated with water was determined. By using quantum-mechanical density functional level of theory (DFT) calculations, the most probable structures of this complex were derived.

Keywords Receptors · Macrocycles · Complexation · DFT · Structure

Introduction

Hexaarylbenzene (HAB) derivatives attract great attention because of their unique propeller-shaped structure and potential applications in molecular electronics and nanotechnology. It has previously been described by employing nuclear magnetic resonance (NMR) spectroscopy and X-ray crystallography that the HAB-based receptor **1** (Scheme 1) binds a single potassium cation because it interacts both with the polar ethereal fence and with the central benzene ring via cation–π interaction [1]. Cation–π interaction is a well-established phenomenon in gas phase and in solid state [2] and is known to play an important role in the stabilization of tertiary structures of various proteins [3].

The dicarbollylcobaltate anion [4] and some of its halogen derivatives are very useful reagents for extraction of various metal cations (especially Cs^+, Sr^{2+}, Ba^{2+}, Eu^{3+}, and Am^{3+}) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes [5–28] and on the technological scale for separation of some high-activity isotopes in reprocessing of spent nuclear fuel and acidic radioactive waste [29–31].

Recently, protonation of valinomycin, some calix[4]arenes, and dibenzo-18-crown-6 has been investigated [32–40]. In the current work, the stability constant of the HAB-based receptor·H_3O^+ (**1**·H_3O^+) complex species is determined in the organic phase of the water/nitrobenzene extraction system. Moreover, by applying quantum-mechanical density functional level of theory (DFT) calculations, the most probable structures of this cationic complex species are derived.

Results and discussion

Extraction experiments

With regard to previous results [32, 41–44], the two-phase water–HCl/nitrobenzene–CsDCC–**1** (hexaarylbenzene-based

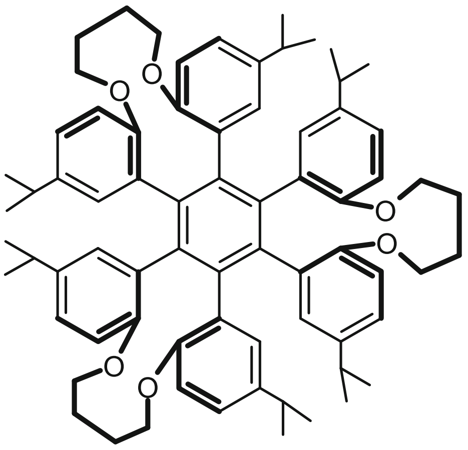
P. Toman
Institute of Macromolecular Chemistry,
Academy of Sciences of the Czech Republic,
Prague, Czech Republic

E. Makrlík (✉)
Faculty of Applied Sciences, University of West Bohemia,
Pilsen, Czech Republic
e-mail: makrlik@centrum.cz

P. Vaňura
Department of Analytical Chemistry,
Faculty of Chemical Engineering, Institute of Chemical
Technology, Prague, Czech Republic

V. Kašička
Institute of Organic Chemistry and Biochemistry,
Academy of Sciences of the Czech Republic,
Prague, Czech Republic

R. Rathore
Department of Chemistry, Marquette University,
Milwaukee, WI, USA



1

Scheme 1

receptor) extraction system (see "Experimental"), chosen for determination of the stability constant of the cationic complex $\mathbf{1}\cdot H_3O^+$ in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium (Eq. 1) to which the equilibrium extraction constant (Eq. 2) corresponds; "aq" and "nb" denote the presence of the species in the aqueous and nitrobenzene phases, respectively.

$$H_3O^+(aq) + \mathbf{1}\cdot Cs^+(nb) \rightleftarrows \mathbf{1}\cdot H_3O^+(nb) + Cs^+(aq);\ K_{ex}(H_3O^+, \mathbf{1}\cdot Cs^+) \tag{1}$$

$$K_{ex}(H_3O^+, \mathbf{1}\cdot Cs^+) = \frac{[\mathbf{1}\cdot H_3O^+]_{nb}[Cs^+]_{aq}}{[H_3O^+]_{aq}[\mathbf{1}\cdot Cs^+]_{nb}}. \tag{2}$$

It is necessary to emphasize that **1** is a considerably hydrophobic receptor, practically present in the nitrobenzene phase only, where this receptor forms—with H_3O^+ and Cs^+—the relatively stable complexes $\mathbf{1}\cdot H_3O^+$ and $\mathbf{1}\cdot Cs^+$.

Taking into account the conditions of electroneutrality in the aqueous and organic phases of the system under study, the mass balances of H_3O^+ and Cs^+ ions at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of cesium, $D_{Cs} = [\mathbf{1}\cdot Cs^+]_{nb}/[Cs^+]_{aq}$, combined with Eq. 2, we get the final expression for the above-mentioned extraction constant (Eq. 3); $C_{HCl}^{in,aq}$ is the initial concentration of HCl in the aqueous phase and $C_{CsDCC}^{in,nb}$ denotes the initial concentration of CsDCC in the organic phase of the system under consideration.

$$K_{ex}(H_3O^+, \mathbf{1}\cdot Cs^+) = \frac{1}{D_{Cs}} \frac{C_{CsDCC}^{in,nb}}{(1 + D_{Cs})C_{HCl}^{in,aq} - C_{CsDCC}^{in,nb}}. \tag{3}$$

From the extraction experiments and γ-activity measurements (see "Experimental"), by using Eq. 3, the following value of the constant $K_{ex}(H_3O^+, \mathbf{1}\cdot Cs^+)$ was determined: $\log K_{ex}(H_3O^+, \mathbf{1}\cdot Cs^+) = -1.4 \pm 0.1$.

Furthermore, with respect to Refs. [4, 41–44], for the exchange extraction constant $K_{ex}(H_3O^+, Cs^+)$ corresponding to the equilibrium $H_3O^+(aq) + Cs^+(nb) \rightleftarrows H_3O^+(nb) + Cs^+(aq)$ and for the extraction constant $K_{ex}(H_3O^+, \mathbf{1}\cdot Cs^+)$ defined above, as well as for the stability constants of the complexes $\mathbf{1}\cdot Cs^+$ and $\mathbf{1}\cdot H_3O^+$ in nitrobenzene saturated with water, denoted by $\beta_{nb}(\mathbf{1}\cdot Cs^+)$ and $\beta_{nb}(\mathbf{1}\cdot H_3O^+)$, one obtains Eq. 4.

$$\begin{aligned}\log\beta_{nb}(\mathbf{1}\cdot H_3O^+) = {} & \log\beta_{nb}(\mathbf{1}\cdot Cs^+) \\ & + \log K_{ex}(H_3O^+, \mathbf{1}\cdot Cs^+) \\ & - \log K_{ex}(H_3O^+, Cs^+).\end{aligned} \tag{4}$$

Using the value $\log K_{ex}(H_3O^+, Cs^+) = -3.0$ inferred from Ref. [41], the constant $\log K_{ex}(H_3O^+, \mathbf{1}\cdot Cs^+)$ given above, $\log \beta_{nb}(\mathbf{1}\cdot Cs^+) = 4.7 \pm 0.1$ (Makrlík E et al. unpublished result), and applying Eq. 4, we obtain the stability constant of the $\mathbf{1}\cdot H_3O^+$ complex in water–saturated nitrobenzene at 25 °C as $\log \beta_{nb}(\mathbf{1}\cdot H_3O^+) = 6.3 \pm 0.2$. In this context, it should be noted that the stability constant of the complex species $H_3O^+\cdot L$, where L is 18-crown-6, in nitrobenzene saturated with water is $\log \beta_{nb}(H_3O^+\cdot L) = 7.56$ [45]. This means that, in the mentioned nitrobenzene medium, the stability of the $\mathbf{1}\cdot H_3O^+$ complex under study is somewhat lower than that of the cationic complex species $H_3O^+\cdot L$ (L = 18-crown-6).

Quantum-mechanical calculations

The quantum-mechanical calculations were carried out at the density functional level of theory (DFT, B3LYP functional) using the Gaussian 03 suite of programs [46]. The 6-31G(d) basis set was used, and the optimizations were unconstrained. Although a possible influence of a polar solvent on the detailed structures of **1** and the $\mathbf{1}\cdot H_3O^+$ complex species could be imagined, our quantum-mechanical calculations in similar cases, performed in analogous way, showed very good agreement of experiment with theory [47–52].

In the model calculations, we optimized the molecular geometries of the parent HAB-based receptor **1** and its complex with H_3O^+. The optimized structure of a free receptor **1** having C_3 symmetry, involving a bowl-shaped cavity, which is comprised of an aromatic bottom (i.e., central benzene ring) and an ethereal fence formed by six oxygen atoms from peripheral aryl groups, is illustrated in Fig. 1. The depth of the cavity, i.e., the distance between the mean plane of the aromatic bottom and that of the ethereal fence, is 2.15 Å (1 Å = 0.1 nm); the diameter of this cavity in **1** is 6.19 Å (Fig. 1).

The structures A and B obtained by the full DFT optimizations of the cationic complex species $\mathbf{1}\cdot H_3O^+$ are depicted in Figs. 2 and 3, together with the lengths of the corresponding strong linear hydrogen bonds (in Å). In both

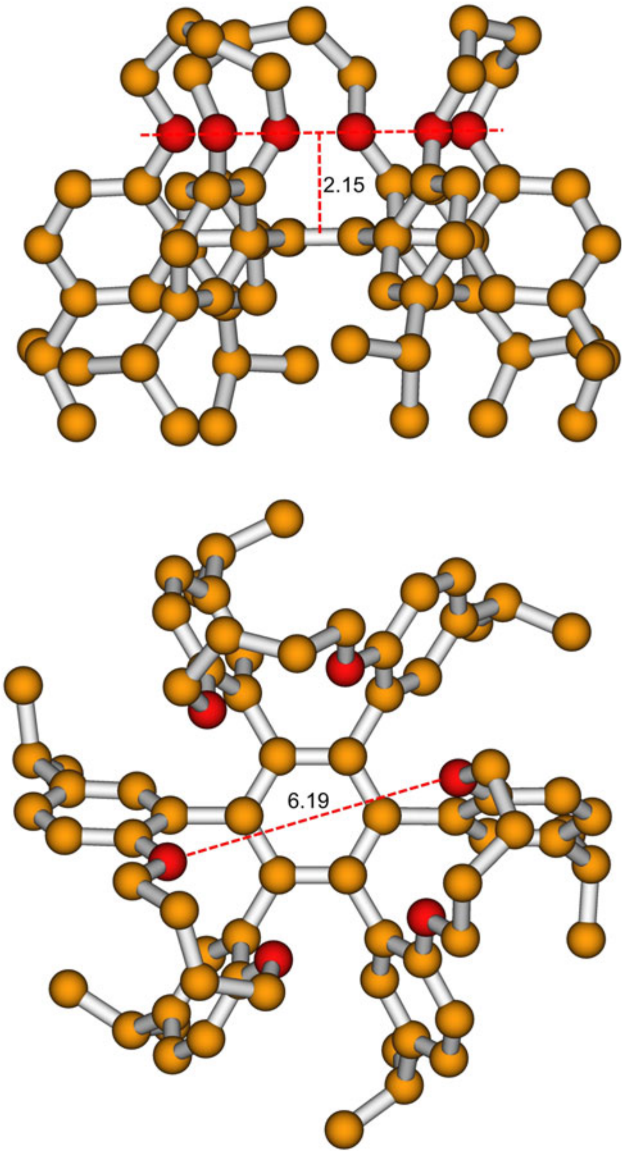


Fig. 1 Two projections of the DFT-optimized structure of free **1** [B3LYP/6-31G(d)] (hydrogen atoms omitted for clarity). The depth of the cavity in **1** is 2.15 Å; the diameter of the cavity in **1** is 6.19 Å

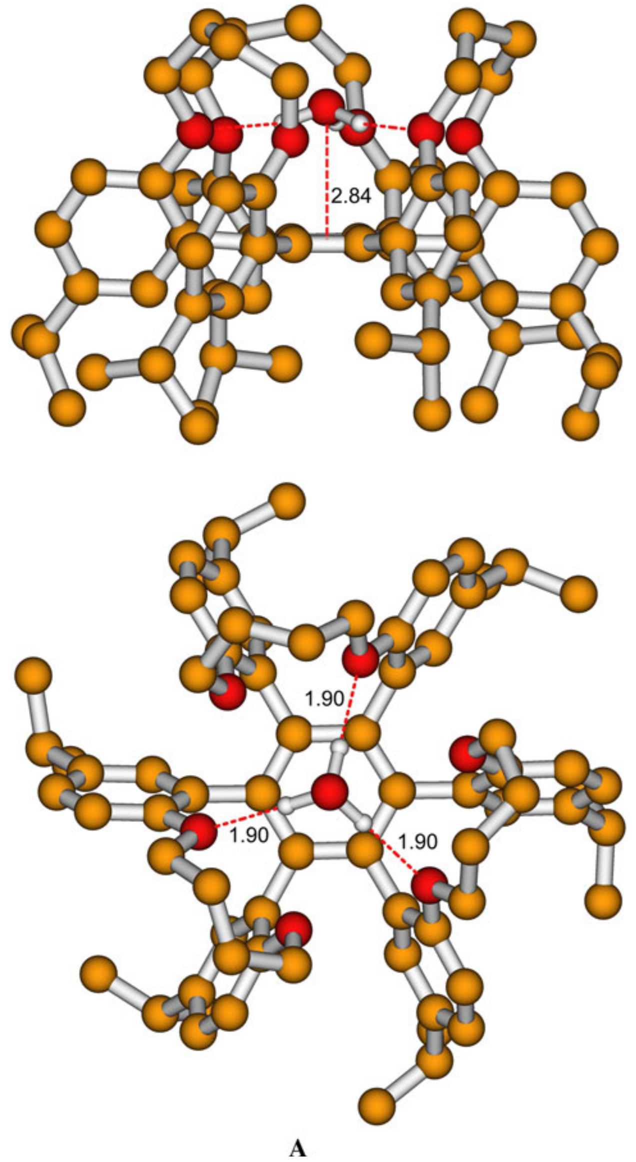
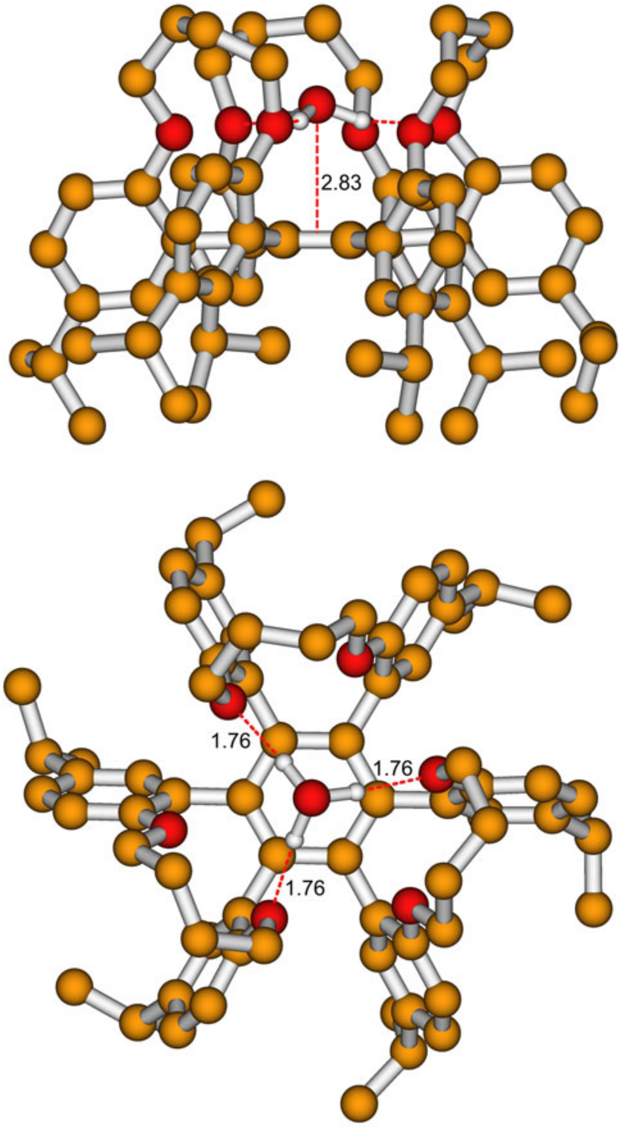


Fig. 2 Two projections of the DFT-optimized structure A of the $\mathbf{1}\cdot H_3O^+$ complex [B3LYP/6-31G(d)] (hydrogen atoms omitted for clarity except those of H_3O^+). The distance between the mean plane of the bottom benzene ring and the oxygen atom of H_3O^+ in the $\mathbf{1}\cdot H_3O^+$ complex is 2.84 Å; H-bond lengths of H_3O^+ to the three corresponding oxygens of the ethereal fence of **1** are 1.90, 1.90, and 1.90 Å; the depth of the cavity in $\mathbf{1}\cdot H_3O^+$ is 2.29 Å; the diameter of the cavity in $\mathbf{1}\cdot H_3O^+$ is 5.83 Å

of these structures of the complex $\mathbf{1}\cdot H_3O^+$ having also C_3 symmetry, the cation H_3O^+ synergistically interacts with the hydrophilic polar ethereal oxygen fence and with the central hydrophobic benzene bottom via cation–π interaction, as pictured in Figs. 2 and 3. Moreover, it is necessary to emphasize that the formation of the complex species $\mathbf{1}\cdot H_3O^+$ results in the tapering of the respective cavity and, at the same time, in its getting longer, as follows from comparison of Fig. 1 with Figs. 2 and 3.

Finally, the interaction energies, $E(\mathrm{int})$, corresponding to the structures A and B of the $\mathbf{1}\cdot H_3O^+$ complex under study [calculated as the differences between the electronic energies of $\mathbf{1}\cdot H_3O^+$ and isolated H_3O^+ and **1** species, $E(\mathrm{int}) = E(\mathbf{1}\cdot H_3O^+) - E(H_3O^+) - E(\mathbf{1})$] are close: −388.5 and −404.0 kJ/mol.

In conclusion, it should be noted that the structures A and B of the $\mathbf{1}\cdot H_3O^+$ complex are apparently in dynamic equilibrium. Besides, from this point of view, the experimentally determined value of the stability constant of $\mathbf{1}\cdot H_3O^+$ in the nitrobenzene medium given above, corresponding to the equilibrium $\mathbf{1}(\mathrm{nb}) + H_3O^+(\mathrm{nb}) \rightleftarrows \mathbf{1}\cdot H_3O^+(\mathrm{nb})$, can be obviously considered as a certain



B

Fig. 3 Two projections of the DFT-optimized structure B of the $\mathbf{1}{\cdot}H_3O^+$ complex [B3LYP/6-31G(d)] (hydrogen atoms omitted for clarity except those of H_3O^+). The distance between the mean plane of the bottom benzene ring and the oxygen atom of H_3O^+ in the $\mathbf{1}{\cdot}H_3O^+$ complex is 2.83 Å; H-bond lengths of H_3O^+ to the three corresponding oxygens of the ethereal fence of **1** are 1.76, 1.76, and 1.76 Å; the depth of the cavity in $\mathbf{1}{\cdot}H_3O^+$ is 2.32 Å; the diameter of the cavity in $\mathbf{1}{\cdot}H_3O^+$ is 5.81 Å

"average" stability constant of the two DFT-calculated structures.

Experimental

Preparation of the electroneutral HAB-based receptor **1** (Scheme 1) is described elsewhere [1]. Cesium dicarbollylcobaltate (CsDCC) was synthesized by means of the method published by Hawthorne et al. [53]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent-grade purity. The radionuclide $^{137}Cs^+$ (Techsnaveksport, Russia) was of standard radiochemical purity.

The extraction experiments were carried out in 10-cm^3 glass test-tubes with polyethylene stoppers: 2 cm^3 of an aqueous solution of HCl of a concentration in the range from 1×10^{-3} to 3×10^{-3} M and microamounts of $^{137}Cs^+$ were added to 2 cm^3 of a nitrobenzene solution of **1** and CsDCC, whose initial concentrations also varied from 1×10^{-3} to 3×10^{-3} M (in all experiments, the initial concentration of **1** in nitrobenzene, $C_1^{\mathrm{in,nb}}$, was equal to the initial concentration of CsDCC in this medium, $C_{\mathrm{CsDCC}}^{\mathrm{in,nb}}$). The test-tubes filled with the solutions were shaken for 2 h at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1-cm^3 samples were taken from each phase, and their γ-activities were measured using a well-type NaI(Tl) scintillation detector connected to a γ-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of cesium, D_{Cs}, were determined as the ratios of the measured radioactivities of $^{137}Cs^+$ in the nitrobenzene and aqueous samples.

Acknowledgments This work was supported by the Czech Ministry of Education, Youth, and Sports, projects MSM 4977751303 and MSM 6046137307. Computer time at the MetaCentrum (project MSM 6383917201), as well as at the Institute of Physics (computer Luna/Apollo), Academy of Sciences of the Czech Republic, is gratefully acknowledged.

References

1. Shukla R, Lindeman SV, Rathore R (2006) J Am Chem Soc 128:5328
2. Ma JC, Dougherty DA (1997) Chem Rev 97:1303
3. Sakurai K, Mizuno T, Hiroaki H, Gohda K, Oku J, Tanaka T (2005) Angew Chem Int Ed 44:6180
4. Makrlík E, Vaňura P (1985) Talanta 32:423
5. Makrlík E, Vaňura P, Selucký P (2009) J Solut Chem 38:1129
6. Valentová Z, Makrlík E (2007) Acta Chim Slov 54:175
7. Makrlík E, Vaňura P, Selucký P (2008) Acta Chim Slov 55:430
8. Makrlík E, Vaňura P, Selucký P (2009) Acta Chim Slov 55:223
9. Makrlík E, Budka J, Vaňura P (2009) Acta Chim Slov 56:278
10. Makrlík E, Vaňura P, Selucký P, Babain VA, Smirnov IV (2009) Acta Chim Slov 56:718
11. Makrlík E, Vaňura P, Selucký P (2009) Acta Chim Slov 56:475
12. Makrlík E, Vaňura P (2007) Z Phys Chem 221:881
13. Makrlík E, Vaňura P (2009) Z Phys Chem 223:247
14. Makrlík E, Vaňura P, Selucký P (2009) Z Phys Chem 223:253
15. Makrlík E, Dybal J, Vaňura P (2009) Z Phys Chem 223:713
16. Makrlík E, Vaňura P, Selucký P, Hálová J (2007) J Radioanal Nucl Chem 274:625
17. Makrlík E, Vaňura P (2008) J Radioanal Nucl Chem 275:217
18. Makrlík E, Vaňura P, Selucký P (2008) J Radioanal Nucl Chem 275:229
19. Makrlík E, Vaňura P, Budka J (2008) J Radioanal Nucl Chem 275:463

20. Makrlík E, Vaňura P, Selucký P (2008) J Radioanal Nucl Chem 275:309
21. Makrlík E, Vaňura P (2008) J Radioanal Nucl Chem 275:673
22. Makrlík E, Vaňura P, Selucký P (2009) J Radioanal Nucl Chem 279:137
23. Makrlík E, Vaňura P, Selucký P (2009) J Radioanal Nucl Chem 279:287
24. Dybal J, Makrlík E, Vaňura P (2009) J Radioanal Nucl Chem 279:553
25. Makrlík E, Vaňura P, Selucký P, Babain VA, Smirnov IV (2009) J Radioanal Nucl Chem 279:743
26. Makrlík E, Vaňura P, Sedláková Z (2009) J Radioanal Nucl Chem 280:607
27. Makrlík E, Vaňura P, Selucký P (2009) J Radioanal Nucl Chem 281:547
28. Makrlík E, Vaňura P, Selucký P (2009) J Radioanal Nucl Chem 281:633
29. Law JD, Brewer KN, Herbst RS, Todd TA, Wood DJ (1999) Waste Manage 19:27
30. Romanovskiy VN, Smirnov IV, Babain VA, Todd TA, Herbst RS, Law JD, Brewer KN (2001) Solvent Extr Ion Exch 19:1
31. Law JD, Herbst RS, Todd TA, Romanovskiy VN, Babain VA, Esimantovskiy VM, Smirnov IV, Zaitsev BN (2001) Solvent Extr Ion Exch 19:23
32. Makrlík E, Vaňura P (2006) Monatsh Chem 137:157
33. Makrlík E, Vaňura P (2006) Monatsh Chem 137:1185
34. Dybal J, Makrlík E, Vaňura P (2007) Monatsh Chem 138:541
35. Kříž J, Dybal J, Makrlík E, Budka J, Vaňura P (2007) Monatsh Chem 138:735
36. Dybal J, Makrlík E, Vaňura P, Selucký P (2007) Monatsh Chem 138:1239
37. Dybal J, Makrlík E, Vaňura P, Budka J (2008) Monatsh Chem 139:1175
38. Dybal J, Makrlík E, Budka J, Vaňura P (2008) Monatsh Chem 139:1353
39. Makrlík E, Dybal J, Vaňura P (2009) Monatsh Chem, 140:29
40. Makrlík E, Vaňura P, Budka J (2009) Monatsh Chem 140:583
41. Rais J (1971) Collect Czech Chem Commun 36:3253
42. Daňková M, Makrlík E, Vaňura P (1997) J Radioanal Nucl Chem 221:251
43. Makrlík E, Hálová J, Kyrš M (1984) Collect Czech Chem Commun 49:39
44. Makrlík E, Vaňura P, Daňková M (1999) J Radioanal Nucl Chem 240:579
45. Vaňura P, Juklíková I (1993) Collect Czech Chem Commun 58:483
46. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery Jr JA, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian 03, Revision C. 02, Gaussian Inc., Wallingford, CT
47. Kříž J, Dybal J, Makrlík E (2006) Biopolymers 82:536
48. Kříž J, Dybal J, Makrlík E, Vaňura P, Lang J (2007) Supramol Chem 19:419
49. Kříž J, Dybal J, Makrlík E, Vaňura P (2008) Supramol Chem 20:387
50. Kříž J, Dybal J, Makrlík E, Budka J, Vaňura P (2008) Supramol Chem 20:487
51. Kříž J, Dybal J, Makrlík E, Budka J (2008) J Phys Chem A 112:10236
52. Kříž J, Dybal J, Makrlík E, Budka J, Vaňura P (2009) J Phys Chem A 113:5896
53. Hawthorne MF, Young DC, Andrews TD, Howe DV, Pilling RL, Pitts AD, Reintjes M, Warren LF, Wegner PA (1968) J Am Chem Soc 90:879