

Controlled self-assembly of bis(crown)stilbenes into unusual bis-sandwich complexes: structure and stereoselective [2 + 2] photocycloaddition†

Sergey P. Gromov,^{*a} Artem I. Vedernikov,^a Natalia A. Lobova,^a
Lyudmila G. Kuz'mina,^b Stepan S. Basok,^c Yuri A. Strelenko,^d
Michael V. Alfimov^a and Judith A. K. Howard^e

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It was shown by ¹H NMR spectroscopy that symmetrical bis(crown)stilbenes (L) and small alkali and alkaline-earth metal cations form 1(L) : 1(M^{m+}) and 1(L) : 2(M^{m+}) complexes in MeCN solutions. In the case of large or hydrated metal cations such as Cs⁺, Rb⁺, K⁺, Ba²⁺, Sr²⁺, [Ca(H₂O)₆]²⁺ and stilbenes with a small crown-ether cavity as compared with the metal cation size, stable bis-sandwich complexes 2(L) : 2(M^{m+}) can also be formed. A stable bis-pseudosandwich 2 : 2 complex is also produced from bis(18-crown-6)stilbene with the propanediammonium ion. The effect of the crown-ether size and the cation size and nature on the route of stilbene phototransformation and product composition was elucidated. The bis-(pseudo)sandwich complexes undergo effective stereoselective [2 + 2] photocycloaddition giving mainly *rcct* isomers of new 1,2,3,4-tetracrown cyclobutanes. The structures of complexes of bis(crown)stilbenes and obtained cyclobutanes were confirmed by X-ray diffraction.

Introduction

Stilbenes and their analogues containing a 1,2-di(aryl/hetaryl)-ethylene structural fragment are the subjects of numerous studies as they possess remarkable spectral fluorescence and photochemical properties such as the ability to undergo

reversible *E/Z* isomerization, electrocyclization, and [2 + 2] photocycloaddition (PCA).¹ These properties were used to design optoelectric media and obtain multiphoton absorption materials for lasers and proposed for optical information recording and storage systems, molecular electronic devices, switches and machines.²

The effect of supramolecular self-assembly of unsaturated compounds on their photochemical properties is of particular interest due to the possibility of controlling the route of photo-reactions in such systems and often also their stereochemical outcome.^{1a,3} For example, stereoselective PCA of stilbene derivatives can occur in the cucurbit[8]uril and γ -cyclodextrin cavities and assist by crown ethers with great macrocycle size.^{3c,4}

For stilbenes containing a crown-ether moiety, self-assembly in the presence of metal or ammonium cations can also be controlled rather easily *via* complexation. For example, bis-sandwich complexes of bis(15-crown-5)- or bis(18-crown-6)stilbenes [(*E*)-**1b** and (*E*)-**1c**] with K⁺ or Cs⁺ ions, respectively, were assumed to form; their structure was not determined.⁵ In the presence of metal cations with large ion diameter (K⁺, Rb⁺, Sr²⁺, Ba²⁺), bis(15-crown-5)oligophenylene-ethylenes form stacked complexes of different structures and stoichiometries in which stereospecific polyPCA takes place.⁶ The stereospecific PCA in the ammonium-containing mono-(24-crown-8)stilbene dimeric complex was studied.⁷ Unusually stable donor–acceptor complexes were found to be formed from (*E*)-**1c** and diammonium derivatives of viologen analogues. These complexes can serve as fluorescence molecular sensors for alkaline-earth metal cations.⁸

^a Photochemistry Centre, Russian Academy of Sciences, ul. Novatorov 7A-1, Moscow 119421, Russian Federation. E-mail: spgromov@mail.ru; Fax: +7 495 936 1255

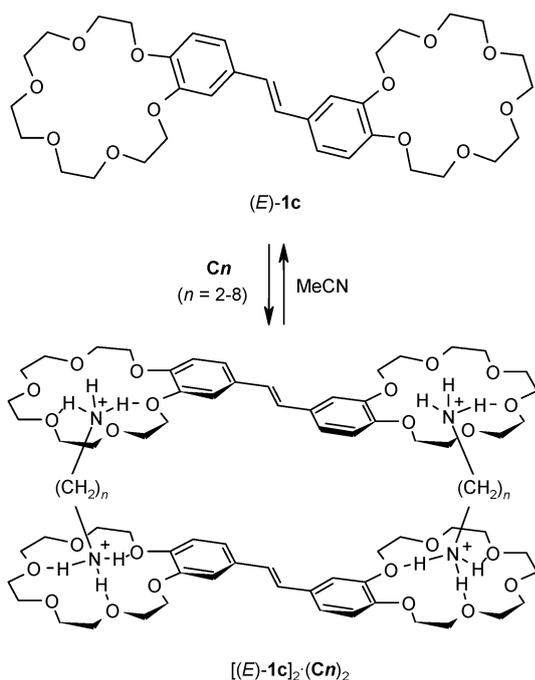
^b N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskiy prosp. 31, Moscow 119991, Russian Federation. E-mail: kuzmina@igic.ras.ru; Fax: +7 495 954 1279

^c A. V. Bogatskiy Physicochemical Institute, National Academy of Sciences of Ukraine, Lustdorfskaya doroga 86, Odessa 65080, Ukraine

^d N. D. Zelinskiy Institute of Organic Chemistry, Russian Academy of Sciences, Leninskiy prosp. 47, Moscow 119991, Russian Federation. E-mail: strel@ioc.ac.ru; Fax: +7 499 135 5328

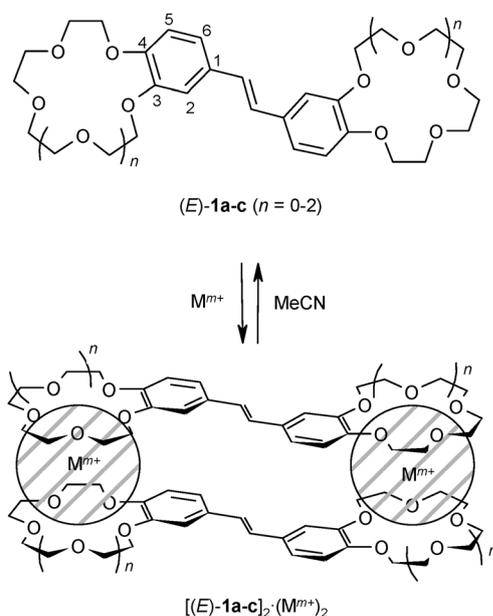
^e Chemistry Department, Durham University, South Road, Durham DH1 3LE, UK. E-mail: j.a.k.howard@durham.ac.uk; Fax: +44 0191 374 3745

† Electronic supplementary information (ESI) available: Combination of conformers of stilbenes (*E*)-**1a–c** within bis-sandwich complexes (Scheme S1). Disorder of stilbene molecules in the crystal (*E*)-**1c**·C3·2.67C₆H₆ and the structure of cyclic trimer (**1c**)₃·(C3)₃ (Fig. S1). Emission spectra of equimolar mixture of (*E*)-**1b** and Ba(ClO₄)₂ and its photolysates after irradiation (Fig. S2). ¹H NMR spectrum of the reaction mixture after photolysis in system (*E*)-**1b**/Ba(ClO₄)₂ (Fig. S3). Absorption spectra of *rcct*-**4b**·(KClO₄)₂, *rcct*-**4c**·(CsClO₄)₂, and a mixture of *rcct*-**4a**·[Ba(ClO₄)₂]₂ and *rtct*-**4a**·[Ba(ClO₄)₂]₂ (Fig. S4). CCDC reference numbers 780035–780041. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00780c



Scheme 1 Formation of bis-pseudosandwich complexes between stilbene (*E*)-**1c** and alkanediammonium ions.

We found that in concentrated solutions, stilbene (*E*)-**1c** can form hydrogen-bonded 2 : 2 bis-pseudosandwich complexes with alkanediammonium salts $\text{H}_3\text{N}^+(\text{CH}_2)_n\text{NH}_3^+ 2\text{ClO}_4^-$ (**Cn**, $n = 2-8$) (Scheme 1); for such complexes with relatively short diammonium ions ($n = 2-4$), effective stereoselective PCA proceeds to give mainly the *rect* isomer of cyclobutane derivative.⁹ However, photoreactions of crown-containing stilbenes are little studied, which is due, not after all other reasons, to the poor accessibility of these compounds.



Scheme 2 Formation of bis-sandwich complexes between stilbenes (*E*)-**1a-c** and large metal cations.

Recently, we developed a simple and convenient synthesis of symmetric bis(crown)stilbenes (*E*)-**1a-c** providing 70–73% yields of these compounds from benzocrown ethers.¹⁰ We suggested that in the presence of appropriate metal cations, these stilbenes would form rather stable bis-sandwich 2 : 2 complexes (Scheme 2) in which the ethylene bonds of two stilbene molecules will be proximate, and, hence, pre-organized for PCA to give cyclobutane derivative. This article presents our ¹H NMR study of the composition and structure of the products of photolysis of **1a-c** in the presence of alkali and alkaline-earth metal cations and compound **C3**. The structures of stilbene complexes of different stoichiometries and also the stereochemistry of the major PCA product, the *rect* isomer of 1,2,3,4-tetracrown cyclobutane, were confirmed by X-ray diffraction study.

Results and discussion

UV/Vis and ¹H NMR studies of stilbene complexes

In MeCN, free stilbenes (*E*)-**1a-c** demonstrate intense long-wavelength absorption (LA) with λ_{max} at ~ 335 nm and fluorescence with a maximum at ~ 385 nm (e.g., Fig. 1, curves 1 and 3). Previously, we found that under these conditions, stilbene (*E*)-**1c** fluorescence has a quantum yield of 0.30.¹¹ The addition of excess alkali (Li, Na, K, Rb, Cs) or alkaline-earth (Mg, Ca, Sr, Ba) metal perchlorate to a solution of **1a-c** induced a hypsochromic shift of the LA maximum ($\Delta\lambda_{\text{max}}$ up to 15 nm) and a slight decrease in its intensity, the most pronounced changes being observed for double-charged metal cations (e.g., Fig. 1, curve 2). This is a usual behaviour for the formation of host-guest complexes of chromogenic crown compounds^{8c,12} and this is obviously caused by the electron-withdrawing effect of cations coordinated by the crown-ether fragments of **1a-c**.

A ¹H NMR study of MeCN-*d*₃ solutions of mixtures of (*E*)-**1a-c** with salts of Group I and II metals demonstrated that the spectral changes depend considerably on the size of the crown-ether cavity of the ligand and the metal cation size. In all cases, the signals of most methylene groups of macrocycles **1a-c** underwent a downfield shift ($\Delta\delta_{\text{H}}$ up to 0.40 ppm) upon

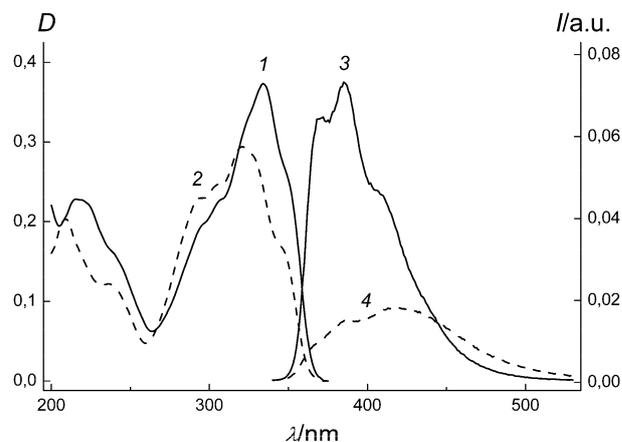


Fig. 1 Absorption (1, 2) and emission (3, 4) spectra of (1, 3) (*E*)-**1b** ($C = 1 \times 10^{-5}$ M) and (2, 4) its equimolar mixture with $\text{Ba}(\text{ClO}_4)_2$ (MeCN, 1 cm cell, ambient temperature); excitation at 270 nm.

addition of excess salt to stilbene, thus confirming binding of the crown-ether moiety to the metal cations. Similar effects were observed in our study of complexation of (*E*)-**1c** with **Cn**.⁹ When the size of the macrocycle cavity was roughly the same or larger than the metal cation diameter, the signals of aromatic and ethylene protons of stilbene also underwent monotonic downfield shifts following increase in the C_M/C_1 ratio (e.g., Fig. 2), which was caused by the electron-withdrawing effect of the cation in the complex. Note that in Fig. 2 the nearly linear dependence $\Delta\delta_H - C_{KClO_4}/C_{1c}$ for $C_{KClO_4}/C_{1c} < 2$ and smoothing of the curves at $C_{KClO_4}/C_{1c} \approx 2$ imply the formation of relatively stable complexes **1c**· K^+ and **1c**·(K^+)₂ (see below).

When the size of the macrocycle cavity was smaller than the diameter of the metal cation, the behaviour of the signals of aromatic and ethylene protons was, in most cases, more complex. As an example, Fig. 3 shows the dependence $\Delta\delta_H - C_{CsClO_4}/C_{1c}$. It can be seen that these proton signals of stilbene (*E*)-**1c** shift upfield ($\Delta\delta_H$ up to -0.26 ppm) at $C_{CsClO_4} < C_{1c}$, and then start to vary in the opposite direction at $C_{CsClO_4} > C_{1c}$. This means that as $CsClO_4$ is added to a solution of **1c**, this first gives a relatively stable complex

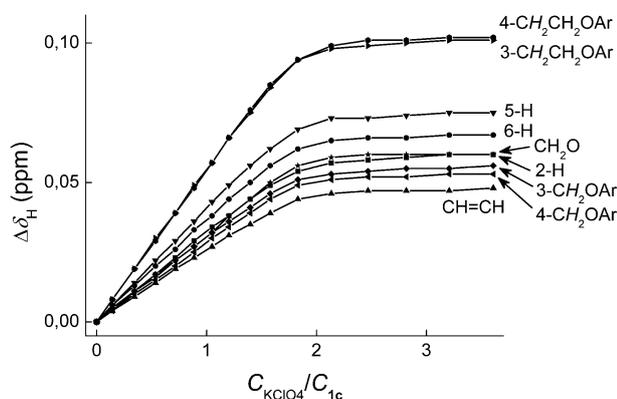


Fig. 2 Values of $\Delta\delta_H = \delta_H(\mathbf{1c}/KClO_4 \text{ mixture}) - \delta_H(\text{free } \mathbf{1c})$ for some protons of (*E*)-**1c** as a function of the $KClO_4/\mathbf{1c}$ concentration ratio ($C_{1c} = 1 \times 10^{-3}$ M, $MeCN-d_3$, 30 °C).

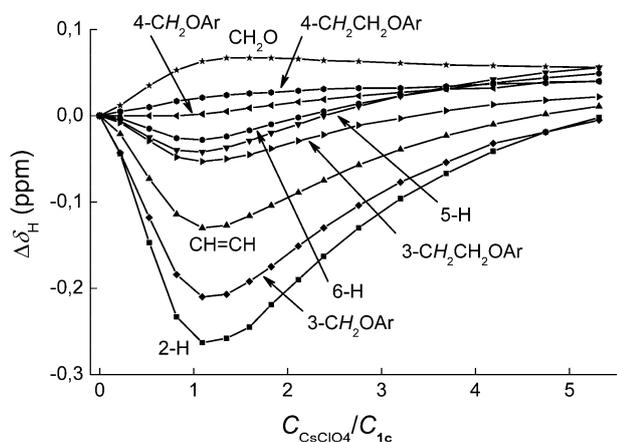


Fig. 3 Values of $\Delta\delta_H = \delta_H(\mathbf{1c}/CsClO_4 \text{ mixture}) - \delta_H(\text{free } \mathbf{1c})$ for some protons of (*E*)-**1c** as a function of the $CsClO_4/\mathbf{1c}$ concentration ratio ($C_{1c} = 1 \times 10^{-3}$ M, $MeCN-d_3$, 30 °C).

1c· Cs^+ , which dimerizes spontaneously to bis-sandwich complex **(1c)₂·(Cs⁺)₂** owing to the possibility of binding large Cs^+ ions simultaneously to two 18-crown-6-ether fragments. In this complex, the conjugated fragments of two stilbene molecules are stacked one above another (see Scheme 2), which results in mutual shielding of the protons of these fragments typically observed for other stacked supramolecular architectures we studied previously.^{8,13} Further increase in the $CsClO_4$ concentration, evidently, shifts the equilibrium toward complex **1c**·(Cs^+)₂, which tends to show downfield shifts of δ_H with respect to the free ligand.

In the case of formation of very stable bis-sandwich complexes **[(E)-1a-c]₂·(M^{m+})₂**, pronounced broadening of the spectral lines or even appearance of several highly overlapped sets of signals was observed. This is indicative of ligand exchange between several types of complexes that is slow on the ¹H NMR time scale (500 MHz). As an example, Fig. 4a and b presents the change of the spectrum of stilbene (*E*)-**1b** after addition of excess $Ba(ClO_4)_2$. Analysis of the COSY spectrum of the mixture showed that in the field of aromatic protons, signals from at least two unsymmetrically substituted ethylene bonds are present (³ $J_{CH=CH} = 15.9\text{--}16.2$ Hz), which are marked in Fig. 4b. Since the stilbene (*E*)-**1b** structure is symmetric, this is indicative of asymmetric structure of some of the formed complexes **(1b)₂·(Ba²⁺)₂**.

Previously,¹⁰ we found that (*E*)-**1a-c** and (*E*)-3,4,3',4'-tetramethoxystilbene can exist in the crystals as symmetric *s-syn,s-syn* and *s-anti,s-anti* conformers differing in the arrangement of the ethylene bond relative to the crown-ether moiety. In solutions, these conformers occur in fast equilibrium in which the former predominates. This is due to the relatively low (~ 5.6 kcal mol⁻¹) energy barrier to the rotation of the benzene ring around the formally single bond of the ethylene fragment. It is clear that the asymmetric *s-anti,s-syn* conformer

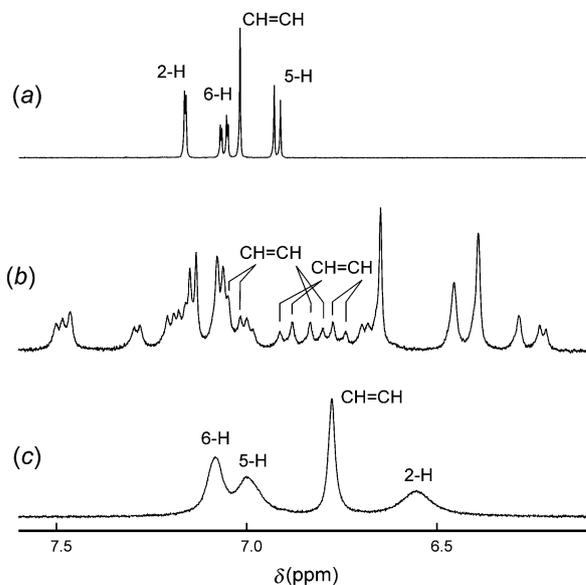
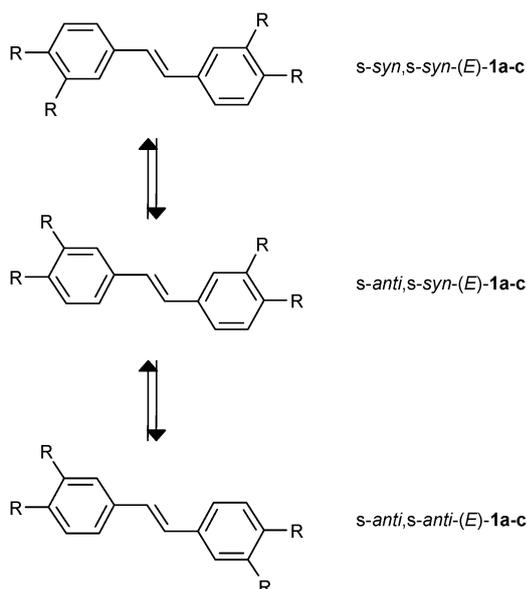


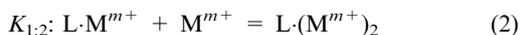
Fig. 4 ¹H NMR spectra (the region for aromatic protons) of (a) (*E*)-**1b** ($C = 5 \times 10^{-3}$ M) and (b, c) its mixture with $Ba(ClO_4)_2$ ($C = 6 \times 10^{-3}$ M) in (a, b) $MeCN-d_3$ and (c) $MeCN-d_3-d_2O$ (10 : 1, v/v) (500 MHz, 30 °C).



Scheme 3 Conformers of stilbenes (*E*)-**1a-c**.

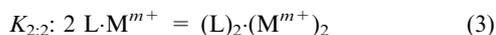
of stilbene should also exist in solution as an intermediate state between the two above-mentioned symmetric conformers (Scheme 3). The bis-sandwich complex can be formed from two identical or different conformers of bis(crown)stilbene, moreover, with either parallel or cross orientation of ethylene bonds (totally 14 types of structures of bis-sandwich complexes, A–N, shown in Scheme S1 in the ESI† to this article). To participate simultaneously in metal cation binding, the crown-ether moieties in such complexes should be located approximately one above another. Since in complexes [(*E*)-**1a-c**]₂·(*M*^{*m*+})₂, the 2-H, 3-CH₂OAr, and CH=CH protons are most shielded (see Fig. 3), some types of complexes can be suggested to predominate in solutions (see types B, D, and I in Scheme S1, ESI†).

The stability constants of complexes formed by stilbenes (*E*)-**1a-c** with metal perchlorates or diammonium compound **C3** were determined by ¹H NMR titration in MeCN-*d*₃. The variation of Δδ_H of the ligand protons vs. the salt-to-ligand concentration ratio for cations whose diameter does not exceed the macrocycle cavity size was adequately described by the model taking into account two equilibria:



where L is stilbene **1a-c**; *K*_{1:1} is the stability constant of complex **1a-c**·*M*^{*m*+}, *M*⁻¹; *K*_{1:2} is the stability constant of complex **1a-c**·(*M*^{*m*+})₂, *M*⁻¹.

When the cation diameter was greater than the macrocycle cavity, it was often necessary to take into account simultaneously equilibria (1), (2), and (3):



where *K*_{2:2} is the stability constant of complex (**1a-c**)₂·(*M*^{*m*+})₂, *M*⁻¹. The stability constants thus found are summarized in

Table 1 Stability constants of complexes of stilbenes (*E*)-**1a-c** with metal and propanediammonium perchlorates^a

<i>M</i> ^{<i>m</i>+} (ClO ₄ ⁻) _{<i>m</i>} , <i>M</i> ^{<i>m</i>+}	log <i>K</i> _{1:1} /log <i>K</i> _{2:2} /log <i>K</i> _{1:2} ^b		
	(<i>E</i>)- 1a	(<i>E</i>)- 1b	(<i>E</i>)- 1c
Na ⁺	2.6/5.0/— ^c	— ^d /— ^c /2.9	— ^d /— ^c /4.0
K ⁺	2.0/— ^c /— ^c	— ^d .e/ > 9 ^e /— ^e	— ^d /— ^c /5.3
Cs ⁺	1.8/— ^c /— ^c	1.6/6.6/— ^c	3.1/8.9/4.3
Ca ²⁺	3.8/— ^c /2.5	— ^d .e/— ^d .e/— ^e	— ^d .e/— ^c /— ^e
Ba ²⁺	4.6/7.0/1.8	— ^d .e/— ^d .e/— ^e	— ^d .e/— ^c /4.7
C3	2.1/— ^c /— ^c	3.1/— ^c /— ^c	— ^d /8.7/1.9

^a ¹H NMR titration, MeCN-*d*₃, 30 ± 1 °C. ^b *K*_{1:1} = [L·M]/([L]·[M]) (*M*⁻¹), *K*_{2:2} = [L₂·M₂]/[L·M]² (*M*⁻¹), *K*_{1:2} = [L·M₂]/([L·M]·[M]) (*M*⁻¹). The total measurement errors of the stability constants were ~30%.

^c NMR titration is inapplicable due to very low (log *K* < 1) value of stability constant. ^d NMR titration is inapplicable due to very high (log *K* > 5) value of stability constant. ^e NMR titration is inapplicable due to slow ligand exchange on the ¹H NMR time scale.

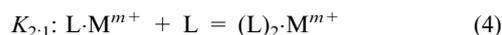
Table 1. Note that in some cases we failed to determine the stability constants of L·*M*^{*m*+} as they were too high and above the upper limit of applicability of ¹H NMR titration (log *K*_{1:1} > 5) and also because of the above-noted slow ligand exchange on the ¹H NMR time scale.

It follows from the data of Table 1 that bis(18-crown-6)stilbene (*E*)-**1c** forms all three types of complexes with caesium and propanediammonium cations. Obviously, only in the presence of these large cations, can rather stable (log *K*_{2:2} ≥ 8.7) bis-sandwich complex (**1c**)₂·(Cs⁺)₂ and bis-pseudosandwich complex (**1c**)₂·(**C3**)₂ be formed (see Schemes 1 and 2). The latter complex is formed due to complementarity of the primary ammonium group and the 18-crown-6-ether moiety and also to relatively short distance between the two ammonium groups in **C3**, which probably does not prevent stacking interactions between the two planar stilbene fragments in some types of bis-pseudosandwich structures.⁹

Bis(12-crown-4)stilbene (*E*)-**1a** forms 1 : 1 complexes of low stability with alkali metal cations (log *K*_{1:1} ≤ 2.6), the stability of these complexes decreasing following increase in the cation diameter. Therefore, only with sodium cations, was the formation of relatively weak complexes (**1a**)₂·(Na⁺)₂ detected (log *K*_{2:2} = 5.0). With double-charged barium cations, **1a** forms all three types of complexes; however, the formation of complexes **1a**·(Ba²⁺)₂ is hampered (log *K*_{1:2} = 1.8), apparently, due to substantial decrease in the electron-donating properties of the macrocycle oxygen atoms, which are conjugated with the benzene ring, in complex **1a**·Ba²⁺. A similar trend of decreasing the stability of 1(L) : 2(*M*^{*m*+}) complexes compared to 1(L) : 1(*M*^{*m*+}) was also found for stilbenes **1b,c**.

As was to be expected, bis(15-crown-5)stilbene (*E*)-**1b** forms stable (log *K*_{2:2} ≥ 6.6) bis-sandwich complexes with large K⁺, Cs⁺, and Ba²⁺ ions and, conversely, does not form such complexes with a relatively small sodium cation or compound **C3** as the ammonium group is not complementary to the 15-membered macroheterocycle. The slow ligand exchange in the system **1b**·Ba²⁺ (see above) and, evidently, very high stability constants of **1b**·Ba²⁺ and (**1b**)₂·(Ba²⁺)₂ precluded their determination. To accelerate the exchange processes, we gradually added deuterated water to a solution of **1b** and

Ba(ClO₄)₂ mixture. When the MeCN-*d*₃-D₂O ratio of 10 : 1 (v/v) has been attained, the ¹H NMR spectrum exhibits only one set of relatively little broadened signals (Fig. 4c); therefore, these conditions were chosen for determination of the stability constants of **1b** complexes. The stability constants of similar complexes of benzo-15-crown-5 ether (B15C5) were determined under the same conditions for comparison. In this case models taking into account the following equilibria proved to be useful: eqn (1) and (3) for **1b** and eqn (1) and (4) for B15C5:



where $K_{2,1}$ is the stability constant of complex (B15C5)₂·M^{m+}, M⁻¹. The stability constants thus found are summarized in Table 2.

Transition to aqueous acetonitrile resulted, as expected,¹⁴ in a considerable decrease in the stability of all types of complexes compared to the results obtained with anhydrous MeCN-*d*₃. Obviously, this is caused by competitive hydration of the cation, which weakens its ion-dipole interaction with the crown-ether heteroatoms. In the case of highly hydrophilic magnesium and calcium cations, the complexation in a MeCN-*d*₃-D₂O mixture almost does not occur. The stability of 1 : 1 complexes of B15C5 varies in the series Mg²⁺, Ca²⁺ << Sr²⁺ < Ba²⁺ < K⁺ ≈ Na⁺, which is correlated with the decrease in the hydrophilicity of these cations. It is known that B15C5 and its derivatives are also able to form sandwich complexes (L)₂·M^{m+} with large potassium, strontium, and barium cations;^{13a,f} however, the stability of complexes (B15C5)₂·M^{m+} in aqueous MeCN-*d*₃ proved even lower than that for B15C5·M^{m+}. In the presence of K⁺, Sr²⁺, and Ba²⁺ ions, the stilbene derivative can form rather stable complexes **1b**·M^{m+} (log $K_{1,1}$ ≥ 3.0), which are largely dimerized (log $K_{2,2}$ ≥ 4.8). The much higher stability of 1 : 1 and 2 : 2 complexes formed by **1b** and large metal cations compared to 1 : 1 and 2 : 1 complexes formed by B15C5 may be related to (i) benefit of the stacking interactions in bis-sandwich complexes and (ii) cumulative effect caused by the presence of two crown-ether fragments in stilbene.

Complexes of stilbenes (*E*)-**1a-c** with metal picrates and perchlorates and with compound **C3** were obtained as solids

Table 2 Stability constants of complexes of stilbene (*E*)-**1b** and benzo-15-crown-5 ether (B15C5) with metal and propanediammonium perchlorates^a

M ^{m+} (ClO ₄ ⁻) _m , M ^{m+}	(<i>E</i>)- 1b log $K_{1,1}$ /log $K_{2,2}$ ^b	B15C5 log $K_{1,1}$ /log $K_{2,1}$ ^b
Na ⁺	1.9/— ^c	2.9/— ^c
K ⁺	3.0/7.4	2.8/2.4
Mg ²⁺	— ^c /— ^c	— ^c /— ^c
Ca ²⁺	— ^c /— ^c	— ^c /— ^c
Sr ²⁺	3.2/4.8	1.8/1.7
Ba ²⁺	3.9/6.1	2.5/2.2
C3	1.3/— ^c	1.4/— ^c

^a ¹H NMR titration, MeCN-*d*₃-D₂O (10 : 1, v/v), 30 ± 1 °C.

^b $K_{1,1} = [L \cdot M] / ([L] \cdot [M])$ (M⁻¹), $K_{2,2} = [L_2 \cdot M_2] / [L \cdot M]^2$ (M⁻¹), $K_{2,1} = [L_2 \cdot M] / ([L \cdot M] \cdot [L])$ (M⁻¹). The total measurement errors of the stability constants were ~30%. ^c NMR titration is inapplicable due to very low value of stability constant (log $K < 1$).

by slow saturation of acetonitrile solutions of a components mixture by benzene or benzene-dioxane vapour; their formal stoichiometry, 1(L) : 1(M^{m+}) or 1(L) : 2(M^{m+}), was confirmed by elemental analysis data (see Experimental section). Note that bis(18-crown-6)stilbene **1c** forms crystalline precipitates of 1(L) : 2(M^{m+}) composition with salts of metal cations having small size as compared with the macrocycle cavity even when the salts are present in equimolar amount in the solution. In the case of stilbene **1b** and salts of metal cations having small size with respect to the 15-membered macrocycle, both 1(L) : 1(M^{m+}) and 1(L) : 2(M^{m+}) crystalline complexes can be obtained.

X-Ray diffraction studies of complexes of stilbenes (*E*)-**1b,c**

Some stilbene complexes were prepared as single crystals, which were studied by X-ray diffractometry. Fig. 5 shows the main components of crystals **1b**·2NaClO₄, **1b**·2Ca(ClO₄)₂·2MeCN·4H₂O, **1b**·KPic·C₆H₆, **1c**·CsPic·C₆H₆, and **1c**·**C3**·2.67C₆H₆ (Pic is the picrate anion). It should be noted that the structure **1b**·2NaClO₄ was determined with high errors due to a bad quality of crystals. However, we included it in the article to show a diversity of the coordination mode of stilbene to a metal cation and do not discuss thin details of its geometry.

The first two structures are 1(L) : 2(M^{m+}) complexes. Each metal cation is coordinated by only one crown-ether fragment; the rest coordination sites are occupied by perchlorate anions or solvent molecules. In spite of somewhat similarity of these structures, they have pronounced distinctions. In **1b**·2NaClO₄, the metal cations are attached at bis(15-crown-5)stilbene on the same side of its mean plane, whereas, in **1b**·2Ca(ClO₄)₂·2MeCN·4H₂O, the metal cations are attached at the ligand on the opposite sides.

In crystal, complex **1b**·2Ca(ClO₄)₂ occupies a special position in the symmetry centre that coincides with the midpoint of the ethylene bond. As a result, the chromophore fragment of stilbene molecule is perfectly planar. In crystal **1b**·2NaClO₄, the stilbene molecule occupies a general position. However, its chromophore fragment is only slightly twisted, the dihedral angle between the benzene rings being 6.4°. This fact together with the planarity of C—O—C_(Ar)—C_(Ar) fragments (the torsion angles are close to 0 or 180°) attest to a relatively high degree of the conjugation over the whole chromophore. Nevertheless, the ethylene bonds in both complexes are essentially localized, which is typical of stilbene derivatives. For both metal complexes **1b**·(M^{m+})₂, the *s-syn,s-syn* conformation of stilbene molecule is found, whereas the *s-anti,s-anti* conformation was revealed for the crystalline free (*E*)-**1b**.¹⁰

The sodium and calcium cations are coordinated by all heteroatoms of the 15-membered macrocycles. Their displacements from the mean plane through the heteroatoms of the nearest macrocycle is only 0.60, 0.68 Å for two independent Na(1), Na(2) ions and 1.14 Å for the Ca(1) ion, *i.e.*, the metal cations are rather deeply immersed into the macroheterocycle cavities of stilbene **1b**. This is well correlated with published data on the compliance of the Na⁺ and Ca²⁺ ion diameters with the 15-crown-5-ether cavity.¹⁵

The coordination sphere of each of Na(1), Na(2) ions also comprises two oxygen atoms of perchlorate anions. In the case

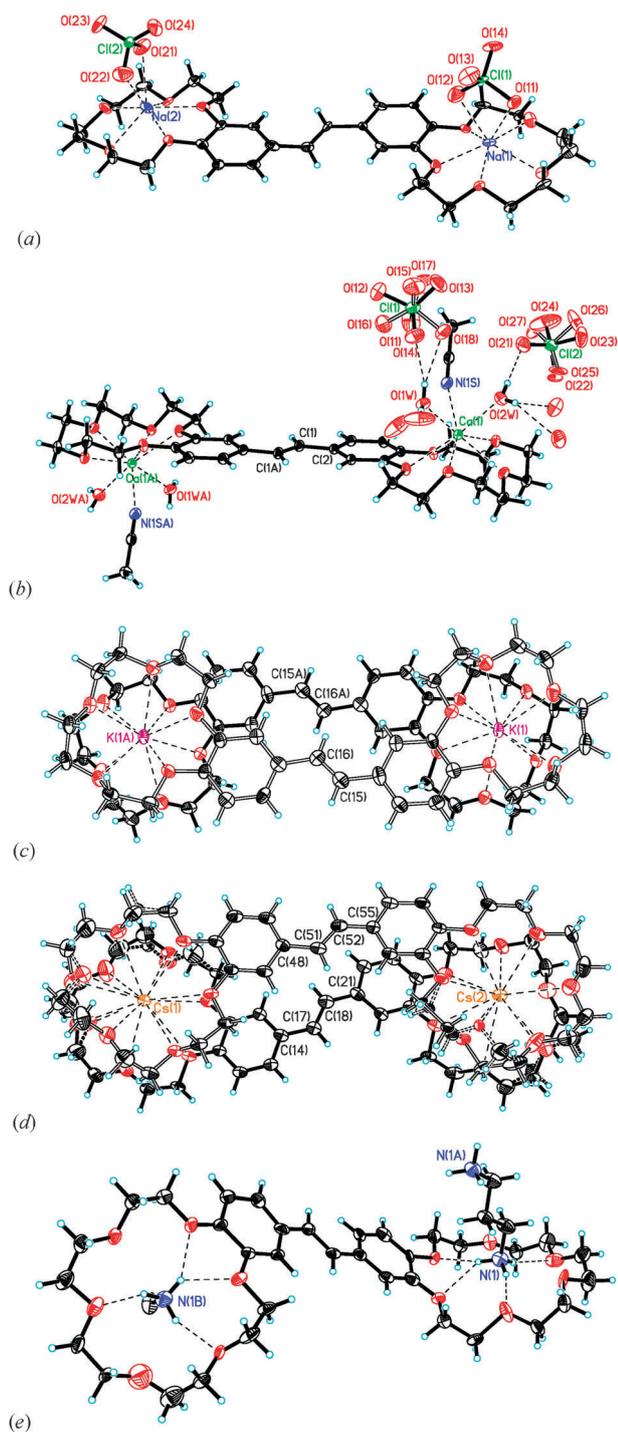


Fig. 5 Structure of the main components of the crystals (a) *(E)*-**1b**·2NaClO₄, (b) *(E)*-**1b**·2Ca(ClO₄)₂·2MeCN·4H₂O, (c) *(E)*-**1b**·KPic·C₆H₆, (d) *(E)*-**1c**·CsPic·C₆H₆, and (e) *(E)*-**1c**·**C3**·2.67C₆H₆. Thermal ellipsoids are drawn at the (a, b) 50, (c, e) 40, or (d) 30% probability level. The additional letters “A” and “B” indicate that atoms belong to symmetrically related positions. Coordination bonds and hydrogen bonds are drawn with dash lines.

of the complex with Ca²⁺ ions, the cation coordination sphere is completed by two water and one MeCN molecules. This type of the coordination is also encountered in the complexes of calcium cations with benzo-15-crown-5-ether derivatives in crystal.¹⁶

Our attempts to grow single crystals of 2(L) : 2(M^{m+}) complexes of stilbenes (*E*)-**1a–c** with K, Cs, Sr, Ba perchlorates suitable for X-ray diffraction failed; the crystals formed were of too high mosaicity. This obstacle has been overcome by replacing the relatively small ClO₄[−] anion for the more bulky picrate anion. Complexes **1b**·KPic and **1c**·CsPic are examples of bis-sandwich structures (types F and K, respectively, in Scheme S1, ESI†), in which stilbene molecule **1b** is represented by *s-anti,s-syn* conformer and two independent molecules **1c** are shown as *s-anti,s-syn* and *s-syn,s-syn* conformers.

In both bis-sandwich complexes, the chromophore fragments are nearly planar: the dihedral angles between the benzene ring planes are 14.5° in **1b**·KPic and 11.9, 9.0° in **1c**·CsPic. As in the previous structures, the ethylene bonds in both complexes are essentially localized.

In **1b**·KPic, the bis-sandwich complex is located in a symmetry centre; therefore, the ethylene bonds and the mean planes of the stilbene chromophore fragments are strictly parallel. The intermolecular C··C distances between the adjacent ethylene fragments, C(15)··C(16A) and C(16)··C(15A), are equal to 4.56 Å. With this geometry, the overlapping of these fragments of the conjugated system is actually lacking. In **1c**·CsPic, the bis-sandwich complex is nonsymmetric; it occupies a general position in the crystal unit cell. The mean planes of the chromophores of two independent stilbene molecules are inclined to each other by angle 2.5° and the ethylene bonds of these fragments are somewhat twisted by ~21°; the C(17)··C(51) and C(18)··C(52) distances between their carbon atoms are 4.03 and 3.93 Å.

The potassium and caesium cations are sandwiched by two macroheterocycles and coordinated by all of their heteroatoms. Displacements of these cations from the mean plane through all heteroatoms of the neighbouring macrocycle are 1.67, 1.66 Å for the K(1) ion and 1.67–1.75 Å for the Cs(1), Cs(2) ions, *i.e.* these large metal cations are positioned approximately above the centres of the macroheterocycle cavities of stilbenes **1b,c**. These parameters are close to analogous characteristics for structurally investigated sandwich complexes between benzo-15-crown-5-ether derivatives and K⁺ ions¹⁷ and between benzo-18-crown-6-ether derivative and Cs⁺ ions.¹⁸

In crystal **1c**·**C3**·2.67C₆H₆, the stilbene molecule is present as its *s-anti,s-syn* conformer. This molecule is disordered over two close positions related by 2-fold axis with equal occupancies. The chromophore fragment is approximately planar—the dihedral angle between the planes of the benzene rings is 12.3°. The 18-crown-6-ether moieties of **1c** coordinate to the NH₃⁺ groups from two dications of compound **C3**, forming normal or bifurcate hydrogen bonds N⁺–H··O(macrocycle). However, instead of expected bis-pseudosandwich structure (**1c**)₂·(**C3**)₂, the components in the crystal form an unusual chiral trimer (**1c**)₃·(**C3**)₃ of the cyclic structure in accordance with the R32 space group (see Fig. S1, ESI†). In this trimer, there are no stacking interactions of the stilbene conjugated systems and, consequently, the PCA reaction is impossible in the solid state. Obviously, in solution such exotic trimer structures can transform to give bis-pseudosandwich complexes, in which the PCA reaction occurs (see below).

Photochemical study of stilbenes (*E*)-**1a–c** and their complexes

The irradiation of MeCN solutions of equimolar mixtures of **1a–c** with salts that form relatively stable 2(L) : 2(M^{m+}) stilbene complexes induced fast changes in the absorption spectra of photolysates, resulting in disappearance of the LA above 300 nm (*e.g.*, Fig. 6). The fluorescence quenching observed during the formation of these complexes (see Fig. 1, curves 2 and 4) continues also during irradiation and results in almost complete disappearance of the emission (*e.g.*, Fig. S2, ESI†). These facts are indicative of the substantial violation of conjugation in the stilbene chromophores as a result of photochemical reactions.

A ¹H NMR study has shown that UV irradiation of solutions of free (*E*)-**1a–c** in MeCN for 2 h gives rise to a mixture of six compounds (Scheme 4, Table 3) with *Z* isomer of stilbene predominating (*cf.* ref. 5 and 9). The photolysates were also found to exhibit signals for phenanthrene derivatives, namely, symmetric *sym*-**2a–c** and asymmetric *asym*-**2a–c**, which are usual products of electrocyclic reactions of (*Z*)-stilbenes followed by oxidation of the intermediate dihydrophenanthrenes with air oxygen.^{1c} The characteristic signals of aromatic protons of compounds **2** appear at δ 7.4–9.2, which is typical of annelated aromatic compounds. The minor products include those formed upon extensive photooxidation, namely, 4'-formylbenzocrown ethers **3a–c** (compound **3c** was also detected previously upon long-term photolysis of **1c** in CH₂Cl₂ in the presence of iodine and air oxygen)⁵ and centrosymmetric derivatives of cyclobutane *rctt*-**4b,c**. The latter compounds are obviously formed from dimeric pairs [(*E*)-**1b,c**]₂, which can be formed owing to the intermolecular stacking interactions of conjugated stilbene fragments. The low yield of *rctt*-**4b,c** (<2 mol%) points to low content of dimeric pairs [(*E*)-**1b,c**]₂ in solution under these conditions.

Under comparable conditions, experiments on irradiation of solutions (*E*)-**1a–c** in the presence of Group I and II metal perchlorates and diammonium compound **C3** were carried out. Data on the compositions and the ratio of photolysis products are summarized in Table 3.

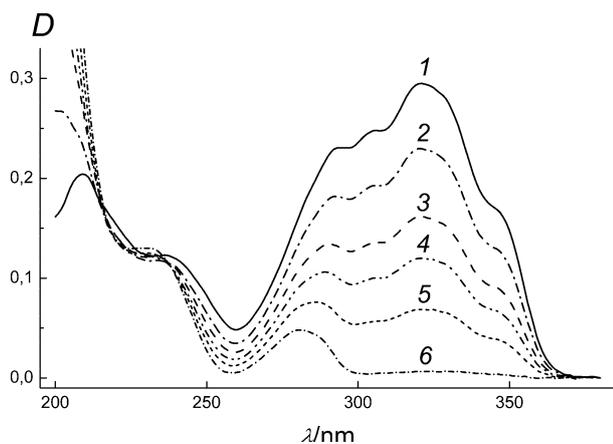
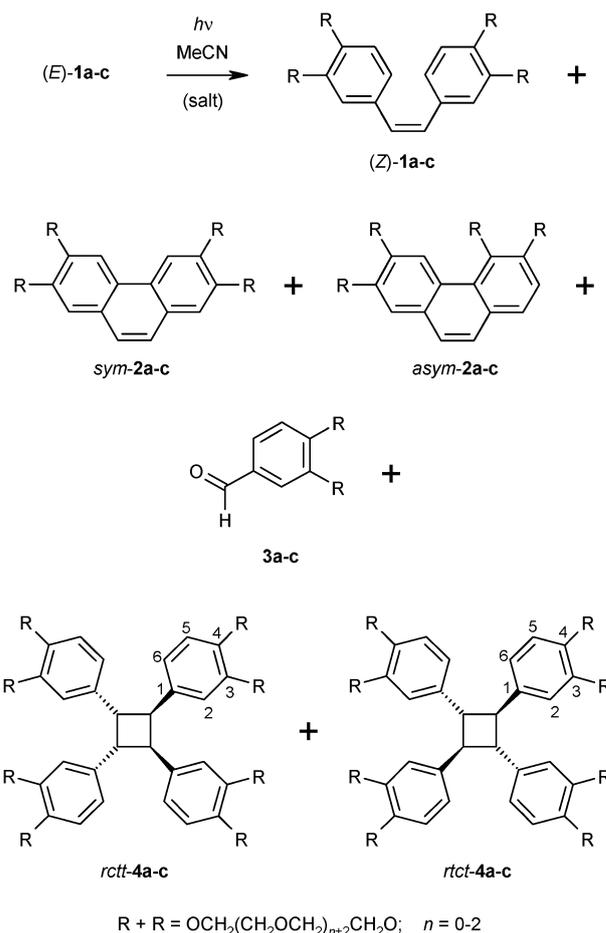


Fig. 6 Absorption spectra of (1) equimolar mixture of (*E*)-**1b** and Ba(ClO₄)₂ (*C* = 1 × 10⁻⁵ M, MeCN, 1 cm cell, ambient temperature) and its photolysates after irradiation over (2) 0.8, (3) 2, (4) 3, (5) 5, and (6) 25 s.



Scheme 4 Photolysis products of stilbenes **1a–c**.

It was found that the presence of cations that are complexed with stilbenes **1a–c** (log *K*_{1:1} > 5) to form relatively stable complexes **1·M^{m+}**, which do not tend to dimerize to bis-sandwich structures, resulted only in suppression of oxidative processes and, as a consequence, in increase in the content of (*Z*)-**1** in the photolysate. Apparently, the complexation with the cation prevents both intramolecular electrocyclic reactions of stilbene and its participation in the intermolecular [2+2] photocycloaddition due to the Coulomb repulsion of the positively charged complexes in the dimeric pair [(*E*)-**1**]₂·(M^{m+})₂, which should precede the formation of **4**.

Conversely, in the presence of metal cations complexed with stilbenes to give fairly stable complexes such as (*E*)-**1·M^{m+}** and [(*E*)-**1**]₂·(M^{m+})₂ (log *K*_{1:1} ≥ 4.6, log *K*_{2:2} ≥ 7.0), cyclobutane derivatives *rctt*-**4a–c** were the major photoproducts formed in the reaction (64–85 mol%) as a result of PCA in bis-sandwich complexes with the conjugated fragments being located approximately one above another and the ethylene bonds being parallel. Note that in these systems, the formation of oxidation products **2** and **3** sharply decreases often down to their total absence in the reaction mixture. This attests indirectly to the relatively high content of bis-sandwich complexes and high efficiency of PCA in them. This is probably possible owing to rather close arrangement of the ethylene bonds in these complexes favourable for cycloaddition, *i.e.*, their pre-organization for PCA. Apart from (*Z*)-**1a–c** and

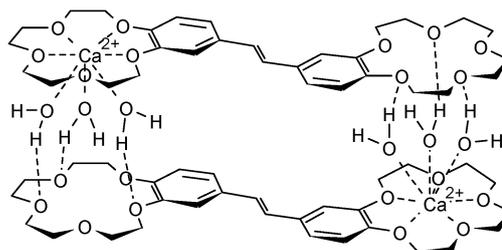
Table 3 Composition and the ratio of the photolysis products of stilbene **1a–c** solutions in the absence and presence of metal and propanediammonium perchlorates^a

Stilbene	Salt, M ^{m+}	Photolysate composition (mol%) ^b						
		(E)-1	(Z)-1	sym-2	asym-2	3	rett-4	rtct-4
1a	— ^c	8.6	73.1	11.0	6.3	1.0	0	0
	Li ⁺	10.2	67.5	10.5	8.9	2.9	0	0
	Na ⁺	8.5	62.1	12.9	8.6	0.7	7.2	0
	K ⁺	11.4	58.0	12.7	13.4	4.5	0	0
	Cs ⁺	10.1	61.3	13.2	11.7	3.7	0	0
	Mg ²⁺	11.7	61.7	13.7	8.6	4.3	0	0
	Ca ²⁺	10.2	84.6	4.1	1.0	0.1	0	0
	Ba ²⁺	1.8	6.9	1.9	0.7	2.1	64.0	22.6
1b	— ^c	12.8	55.6	17.8	7.8	4.4	1.6	0
	Li ⁺	12.5	65.3	11.1	7.7	3.4	0	0
	Na ⁺	12.3	68.5	9.6	6.9	2.7	0	0
	K ⁺	0	0	0	0	0	84.0	16.0
	Rb ⁺	3.1	0	3.5	2.3	2.0	82.9	6.2
	Cs ⁺	7.2	35.7	18.9	9.3	6.4	19.5	3.0
	Mg ²⁺	8.0	55.7	5.1	0	0	28.4	2.8
	Ca ²⁺	0	20.0	0	0	0	76.9	3.1
	Sr ²⁺	0	0	0	0	0	85.5	14.5
	Ba ²⁺	0	0	0	0	0	74.1	25.9
	C3	6.2	77.2	5.4	0	6.2	5.0	0
	1c	— ^{c,d}	12.4	55.0	17.5	8.1	5.1	1.9
K ⁺		13.6	67.0	8.7	7.3	3.4	0	0
Rb ⁺		12.8	62.9	13.5	6.6	4.2	0	0
Cs ⁺		1.1	3.3	3.7	0.7	1.5	73.5	16.2
Ba ²⁺		12.1	73.8	5.3	3.5	2.4	2.9	0
C3 ^d		0	12.6	0	0	0.1	83.8	3.5

^a MeCN, C₁ = 1 × 10⁻³ M, 1.1 equiv. M^{m+}(ClO₄⁻)_m or H₃N⁺(CH₂)₃NH₃⁺ 2ClO₄⁻ (**C3**). ^b According to the ¹H NMR spectral data. ^c Without salt. ^d Data from ref. 9.

major *rett-4a–c*, minor *rtct* cyclobutanes **4a–c** (3–27 mol%) were also detected; obviously, these are formed upon PCA of complexes [(E)-**1a–c**]₂·(M^{m+})₂ with crossed ethylene bonds (for example, see structure of type B in Scheme S1, ESI[†]).

Note unusual photochemical properties of systems **1b**/Ca²⁺(Mg²⁺). In view of the similarity of the cavity size of the 15-membered macrocycle and the metal cation diameters, one could expect the absence of formation of stable 2(L) : 2(M²⁺) complexes and, hence, low content of cyclobutanes **4b** in the photolysis products. Conversely, it was found that cycloaddition of **1b** in the presence of Ca²⁺ ions is only slightly slower than that in the **1b**/Ba²⁺(Sr²⁺) systems, moreover, the selectivity of formation of *rett-4b*/*rtct-4b* is even higher. A similar situation was observed for Mg²⁺ ions but the rate of PCA was considerably lower. Presumably, this unusual behaviour is due to partial hydration of the relatively small alkaline-earth metal cation complexed with the benzo-15-crown-5-ether fragment. As shown by X-ray diffraction study of **1b**·2Ca(ClO₄)₂, the calcium coordination sphere may additionally contain three rather small solvation molecules, for example, water molecules (see Fig. 5b). The hydrogen atoms of these water molecules are directed away from the stilbene **1b** basis molecule, thus creating the binding site for a second stilbene molecule through hydrogen bonding to the oxygen atoms of its free macrocyclic fragment (Scheme 5). Apparently, the complexation in solution involves hydrated ions, [Ca(H₂O)_x]²⁺ or [Mg(H₂O)_x]²⁺ (x = 1–3), whose effective diameter may be even greater than the diameter of



Scheme 5 Possible structure of complex [(E)-**1b**]₂·{[Ca(H₂O)₃]²⁺}₂.

the largest studied barium and caesium cations. The high stereoselectivity of PCA in the systems **1b**/Ca²⁺(Mg²⁺) is attributable to more stringent requirements to the orientation of stilbene molecules in complexes [(E)-**1b**]₂·{[M(H₂O)_x]²⁺}₂, imposed by hydrogen bonding.

The signals of aromatic and cyclobutane protons of cyclobutane isomers, *rett-4a–c* and *rtct-4a–c*, are substantially different (for example, Fig. S3, ESI[†]). This provides reliable identification of the isomers. In a DMSO-*d*₆ solution, all aromatic signals of the *rtct* isomer are shifted downfield (Δδ_H up to 0.26 ppm) with respect to analogous signals of the *rett* isomer, and, conversely, the cyclobutane proton signal for *rtct-4* (singlet at δ ≈ 3.4) is located at higher field than the analogous signal of *rett-4* (singlet at δ ≈ 4.3).⁹ This is a typical spectral behaviour for the corresponding isomers of the 1,2,3,4-tetraaryl-containing cyclobutane¹⁹ caused by the *trans* arrangement relative to each other of all vicinal substituents in the cyclobutane ring of *rtct-4a–c* and mixed, *trans* and *cis* arrangement in the case of *rett-4a–c*.

The major photoproducts in the systems **1b**/KClO₄, **1b**/Ca(ClO₄)₂, **1c**/CsClO₄, and **1c**/C3 were isolated by crystallization as complexes *rett-4b*·(KClO₄)₂, *rett-4b*·[Ca(ClO₄)₂]₂, *rett-4c*·(CsClO₄)₂, and *rett-4c*·(C3)₂, respectively. Their structures were confirmed by ¹H and ¹³C NMR spectroscopy and elemental analysis data. The absorption spectra of these complexes are characterized by disappearing of the absorption at > 300 nm (for example, see Fig. S4, ESI[†]); this confirms the violation of the chromophore conjugation chain in cyclobutane. Free cyclobutanes *rett-4b* and *rett-4c* were prepared by decomplexation of *rett-4b*·[Ca(ClO₄)₂]₂ by ethylenediaminetetraacetic acid in the presence of Me₄NOH and by decomplexation of *rett-4c*·(C3)₂ or *rett-4c*·(C4)₂⁹ in a water–organic solvent mixture (see Experimental section).

X-Ray diffraction studies of metal complexes of cyclobutane *rett-4b*

The structures of two metal complexes of *rett-4b* were determined by X-ray diffraction. Fig. 7 shows the structure of the key components of the crystal unit cells of these complexes.

In crystal *rett-4b*·2KClO₄, the cyclobutane molecule occupies a special position on crystallographic axis 2, which passes through the midpoints of the bonds of the cyclobutane ring, C(1)–C(1A) and C(16)–C(16A). The cyclobutane ring exists in a non-planar conformation: the torsion angles at the C(1)–C(16)–C(16A)–C(1A) ring range from –14.9 to 14.6°. The dihedral angle between the planes of the *cis*-arranged benzene rings is only 23.2°; these rings are proximate in space in such a way that the crown-ether fragments connected to

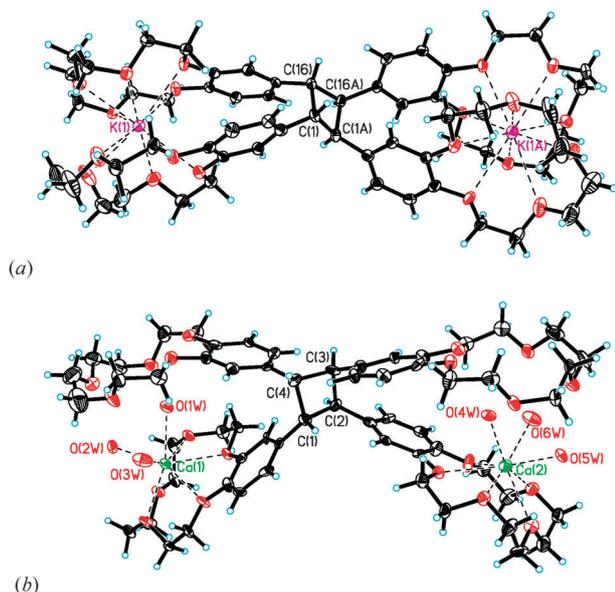


Fig. 7 Structure of the main components of crystals (a) *rctt-4b*·2KClO₄·2C₆H₆·4H₂O and (b) *rctt-4b*·2Ca(ClO₄)₂·3C₆H₆·9H₂O. Thermal ellipsoids are drawn at the 50% probability level. The additional letter “A” indicates that atoms belong to symmetrically related positions. Coordination bonds are drawn with dash lines.

them coordinate the K(1) cation, thus forming an intramolecular sandwich complex. The potassium cation is located almost exactly in the middle between two 15-membered macrocycles and is coordinated by all of their oxygen atoms: the displacements of the cation from the mean planes through all heteroatoms of the two macrocycles are 1.72 and 1.68 Å. These parameters are similar to analogous characteristics of bis-sandwich structure **1b**-KPic·C₆H₆ (see above); apparently, the PCA reaction does not induce considerable steric strain on passing from the initial complex [(*E*)-**1b**]₂·(K⁺)₂ to *rctt-4b*·(K⁺)₂.

In crystal *rctt-4b*·2Ca(ClO₄)₂, the cyclobutane molecule occupies a general position. The cyclobutane ring is non-planar: the torsion angles at the C(1)–C(2)–C(3)–C(4) ring vary from –21.6 to 21.2°. The dihedral angles between the planes of *cis*-arranged benzene rings are 47.6 and 35.6°. These rings are more remote from each other than in the previous structure; therefore, only two crown-ether fragments coordinate relatively small Ca(1) and Ca(2) cations, whereas the other two macrocycles do not participate in their binding. The deviations of cations from the mean plane through all heteroatoms of the nearest macrocycle are 1.15 and 1.11 Å. These parameters are similar to those characteristics of the crystalline complex **1b**·2Ca(ClO₄)₂ (see above). As in the mentioned complex, in this case, the coordination sphere of each independent calcium cation contains three water molecules. Typically, the O(1W),...,O(6W) water molecules connected to calcium cations are located in space between the two *cis*-arranged benzo-15-crown-5-ether fragments. Although the hydrogen atoms of these water molecules were not localized, the shortest O(water)···O(free macrocycle) distances are in the range of 2.72–2.79 Å, which implies the presence of a hydrogen bond network between the indicated water molecules and the oxygen atoms of free macrocycles. Thus, the found structural

characteristics of *rctt-4b*·2Ca(ClO₄)₂ indirectly confirm that bis-sandwich complex [(*E*)-**1b**]₂·{[Ca(H₂O)₃]²⁺}₂ (see Scheme 5) may exist in solution, which should precede the formation of the cyclobutane derivative.

Note that the structure of cyclobutane *rctt-4c* as the complex with diammonium compound **C4** was determined in our recent X-ray diffraction study.⁹ The formation of this compound could have been preceded by bis-pseudosandwich complex [(*E*)-**1c**]₂·(C4)₂, consisting of stilbene *s-syn,s-syn* and *s-anti,s-anti* conformers (structure of type I in Scheme S1, ESI†). From the consideration of the crystal structures of *rctt-4b*·2KClO₄ and *rctt-4b*·2Ca(ClO₄)₂ it follows that the cyclobutane *rctt-4b* might be formed from the bis-sandwich complexes of the same type. Thus, although free stilbenes (*E*)-**1a–c** are highly conformationally flexible and can be assembled in the presence of metal cations or diammonium compounds to bis-(pseudo)sandwich structures with various mutual orientation of chromophores and ethylene bonds, the indirect evidence that the [2+2] photocycloaddition occurs only for one type of complexes to give the *rctt* isomers has been obtained.

Conclusions

Thus, we studied systematically the characteristic features of complexation of symmetric bis(crown)stilbenes with Group I, II metal cations and H₃N⁺(CH₂)₃NH₃⁺ ions and for the first time elucidated their influence on the photoreaction route. Three types of stilbene self-assembly were studied: (i) by means of metal cations, (ii) by means of hydrogen bonds, and (iii) mixed type self-assembly. Large metal cations whose diameter exceeds the size of stilbene macrocycle cavity promote the formation of stable unusual bis-sandwich 2(L) : 2(M^{m+}) complexes, in which two stilbene molecules are located one above another and their ethylene bonds are close in space. Complexes of similar structure are formed by bis(15-crown-5)-stilbene in the presence of hydrated ions, [Ca(H₂O)_x]²⁺, [Mg(H₂O)_x]²⁺, and by bis(18-crown-6)stilbene with propane-diammonium ions. In these complexes, two stilbene molecules are held together through numerous hydrogen bonds. In bis-(pseudo)sandwich complexes, stereoselective [2+2] photocycloaddition takes place to give mainly *rctt* isomers of tetracrown cyclobutanes, which were studied by X-ray diffraction. The identified trends allow one to control the direction of phototransformation of bis(crown)stilbenes, which can be used to obtain new homotetratopic receptors and for optical data recording systems.

Experimental section

General

The melting points were measured with a Mel-Temp II apparatus in a capillary and are uncorrected. The ¹H and ¹³C NMR spectra were recorded on a Bruker DRX500 instrument in DMSO-*d*₆ and MeCN-*d*₃ at 25–30 ° using the solvent as the internal reference (δ_H 2.50 and 1.96, respectively; δ_C 39.43 for DMSO-*d*₆); *J* values are given in Hz. ¹H–¹H COSY and ROESY spectra and ¹H–¹³C COSY (HSQC and

HMBC) spectra were used to assign the proton and carbon signals (see Schemes 2 and 4 for atom numbering). Absorption and emission spectra were recorded on a UV-3101PC spectrophotometer and a RF-5301PC spectrofluorimeter (Shimadzu) in the range of 200–500 and 280–600 nm, respectively, with an increment of 1 nm in MeCN (spectroscopic grade, the water content $\leq 0.03\%$, Cryochrom, Russian Federation) at ambient temperature using 1-cm quartz cells. High resolution ESI mass spectra were measured on a MicrOTOF II instrument (Bruker Daltonics) in the range of $m/z = 50$ –3000 for positive ions (MeCN solution inlet, nitrogen gas flow, 4500 V capillary voltage). Elemental analyses were performed at the microanalytical laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds (Moscow, Russian Federation).

Preparations

Ethylenediaminetetraacetic acid, Me₄NOH (20%, aq.), and water (HPLC grade) were used as received (Aldrich). All metal perchlorates (Aldrich) were dried at 200 °C *in vacuo*. K, Cs, and Ba picrates were obtained by neutralization of aqueous KOH, CsOH, and BaO with a 5% excess of picric acid (Aldrich) followed by evaporation to dryness *in vacuo*, washing with abs. EtOH, and drying in air. Stilbenes (*E*)-**1a–c**,¹⁰ benzo-15-crown-5 ether,²⁰ and salt H₃N⁺(CH₂)₃NH₃⁺ 2ClO₄⁻ (**C3**)^{13d} were obtained according to known procedures.

Complexes between stilbenes (*E*)-**1a–c** and salts (general method)

A solution of a mixture of stilbene (*E*)-**1a–c** and metal perchlorate or picrate (1 or 2 equiv.) or compound **C3** (1 equiv.) in MeCN (3–5 cm³) was slowly saturated with benzene or benzene–dioxane mixture (~2 : 1, v/v) by the vapour diffusion method at ambient temperature in the dark until a precipitate was formed (for 1–2 weeks). The precipitate was separated by decantation and dried at 80 °C *in vacuo*.

Complex [(*E*)-**1a**]₂·[Ba(ClO₄)₂]₂ was obtained from (*E*)-**1a** (9.5 mg, 20.1 μmol) and Ba(ClO₄)₂ (6.6 mg, 19.6 μmol) as a white powder (14.4 mg, 87%); mp > 360 °C (dec.) (Found: C, 39.50; H, 4.03. Calc. for 2C₂₆H₃₂O₈·2BaCl₂O₈·2MeCN: C, 39.57; H, 4.15%).

Complex (*E*)-**1b**·NaClO₄ was obtained from (*E*)-**1b** (20.6 mg, 36.8 μmol) and NaClO₄ (4.5 mg, 36.6 μmol) as small colourless crystals (20.1 mg, 80%); mp > 310 °C (dec.) (Found: C, 52.81; H, 5.92. Calc. for C₃₀H₄₀O₁₀·NaClO₄: C, 52.75; H, 5.90%).

Complex [(*E*)-**1b**]₂·(KClO₄)₂ was obtained from (*E*)-**1b** (9.8 mg, 17.5 μmol) and KClO₄ (2.5 mg, 18.0 μmol) as small colourless crystals (10.9 mg, 89%); mp > 340 °C (dec.) (Found: C, 51.41; H, 5.71. Calc. for 2C₃₀H₄₀O₁₀·2KClO₄: C, 51.53; H, 5.77%).

Complex [(*E*)-**1b**]₂·(KPic)₂ was obtained from (*E*)-**1b** (8.7 mg, 15.5 μmol) and potassium picrate (4.1 mg, 15.4 μmol) as yellow crystals (11.8 mg, 87%); mp 249–251 °C (Found: C, 53.04; H, 5.40; N, 4.61. Calc. for 2C₃₀H₄₀O₁₀·2C₆H₂KN₃O₇·0.5C₆H₆·3H₂O: C, 52.59; H, 5.24; N, 4.91%).

Complex [(*E*)-**1b**]₂·(CsClO₄)₂ was obtained from (*E*)-**1b** (17.8 mg, 31.8 μmol) and CsClO₄ (7.4 mg, 31.8 μmol) as small

colourless crystals (22.3 mg, 88%); mp 274–278 °C (dec.) (Found: C, 45.36; H, 4.98. Calc. for 2C₃₀H₄₀O₁₀·2CsClO₄: C, 45.44; H, 5.08%).

Complex (*E*)-**1b**·Mg(ClO₄)₂ was obtained from (*E*)-**1b** (20.3 mg, 36.3 μmol) and Mg(ClO₄)₂ (8.0 mg, 35.7 μmol) as small colourless crystals (25.9 mg, 93%); mp > 310 °C (dec.) (Found: C, 45.94; H, 5.19. Calc. for C₃₀H₄₀O₁₀·MgCl₂O₈: C, 45.97; H, 5.14%).

Complex (*E*)-**1b**·[Mg(ClO₄)₂]₂ was obtained from (*E*)-**1b** (9.9 mg, 17.7 μmol) and Mg(ClO₄)₂ (8.4 mg, 37.5 μmol) as small colourless crystals (15.9 mg, 89%); mp > 320 °C (dec.) (Found: C, 35.60; H, 4.19. Calc. for C₃₀H₄₀O₁₀·2MgCl₂O₈: C, 35.78; H, 4.00%).

Complex (*E*)-**1b**·[Ca(ClO₄)₂]₂ was obtained from (*E*)-**1b** (11.6 mg, 20.7 μmol) and Ca(ClO₄)₂ (5.0 mg, 20.9 μmol) as colourless crystals (12.3 mg, 100%); mp > 330 °C (dec.) (Found: C, 37.84; H, 4.31. Calc. for C₃₀H₄₀O₁₀·2CaCl₂O₈·C₆H₆·2H₂O: C, 37.51; H, 4.37%).

Complex [(*E*)-**1b**]₂·[Sr(ClO₄)₂]₂ was obtained from (*E*)-**1b** (12.9 mg, 23.0 μmol) and Sr(ClO₄)₂ (6.6 mg, 23.0 μmol) as small colourless crystals (17.2 mg, 88%); mp > 340 °C (dec.) (Found: C, 42.37; H, 4.71. Calc. for 2C₃₀H₄₀O₁₀·2SrCl₂O₈: C, 42.53; H, 4.76%).

Complex [(*E*)-**1b**]₂·[Ba(ClO₄)₂]₂ was obtained from (*E*)-**1b** (12.8 mg, 22.9 μmol) and Ba(ClO₄)₂ (7.8 mg, 23.2 μmol) as small colourless crystals (18.9 mg, 92%); mp > 340 °C (dec.) (Found: C, 39.96; H, 4.38. Calc. for 2C₃₀H₄₀O₁₀·2BaCl₂O₈: C, 40.18; H, 4.50%).

Complex (*E*)-**1c**·(KClO₄)₂ was obtained from (*E*)-**1c** (20.3 mg, 31.3 μmol) and KClO₄ (4.3 mg, 30.9 μmol) as small colourless crystals (14.1 mg, 98%); mp > 285 °C (dec.) (Found: C, 44.41; H, 5.10. Calc. for C₃₄H₄₈O₁₂·2KClO₄: C, 44.11; H, 5.23%).

Complex [(*E*)-**1c**]₂·(CsClO₄)₂ was obtained from (*E*)-**1c** (10.9 mg, 16.8 μmol) and CsClO₄ (4.0 mg, 17.2 μmol) as colourless crystals (12.6 mg, 85%); mp 260–263 °C (dec.) (Found: C, 46.44; H, 5.48. Calc. for 2C₃₄H₄₈O₁₂·2CsClO₄: C, 46.35; H, 5.49%).

Complex [(*E*)-**1c**]₂·(CsPic)₂ was obtained from (*E*)-**1c** (15.2 mg, 23.5 μmol) and caesium picrate (8.4 mg, 23.3 μmol) as small yellow druses (22.1 mg, 91%); mp 210–213 °C (Found: C, 49.74; H, 5.16; N, 3.77. Calc. for 2C₃₄H₄₈O₁₂·2C₆H₂CsN₃O₇·1.5C₆H₆: C, 50.03; H, 5.14; N, 3.93%).

Complex (*E*)-**1c**·[Ba(ClO₄)₂]₂ was obtained from (*E*)-**1c** (6.9 mg, 10.7 μmol) and Ba(ClO₄)₂ (3.6 mg, 10.7 μmol) as a white powder (6.1 mg, 77%); mp > 365 °C (dec.) (Found: C, 33.90; H, 4.05. Calc. for C₃₄H₄₈O₁₂·2BaCl₂O₈·4MeCN: C, 33.96; H, 4.07%).

Complex (*E*)-**1c**·[Ba(Pic)]₂ was obtained from (*E*)-**1c** (2.7 mg, 4.2 μmol) and barium picrate (4.7 mg, 7.9 μmol) as an orange powder (4.7 mg, 62%); mp 207–209 °C (Found: C, 37.94; H, 3.06; N, 8.40. Calc. for C₃₄H₄₈O₁₂·2C₁₂H₄BaN₆O₁₄·0.5C₆H₆·3H₂O: C, 37.98; H, 3.40; N, 8.71%).

Complex [(*E*)-**1c**]₃·(**C3**)₃ was obtained from (*E*)-**1c** (12.2 mg, 18.8 μmol) and compound **C3** (5.1 mg, 18.6 μmol) as colourless crystals (16.4 mg, 92%); mp > 260 °C (dec.) (Found: C, 49.85; H, 6.71; N, 2.77. Calc. for 3C₃₄H₄₈O₁₂·3C₃H₁₂Cl₂N₂O₈·1.5C₆H₆: C, 49.90; H, 6.60; N, 2.91%).

Photolysis of stilbenes (*E*)-1a–c and their complexes with metal perchlorates and salt C3 (general procedure)

A solution of a mixture of (*E*)-1a–c (15.4 μmol) and $\text{M}^{m+}(\text{ClO}_4^-)_m$ or C3 (16.9 μmol) (or without salt) in MeCN (15 cm^3 , spectroscopic grade) was placed in a quartz cell (5 cm \times 4.5 cm \times 1 cm), and the mixture was irradiated for 2 h with stirring with the light from a L8253 xenon lamp (Hamamatsu, maximum power, A9616-05 light filter (transmission 320–420 nm), distance to the light source 10 cm) from the side of the largest facet of the cell. The solvent was thoroughly evaporated *in vacuo* and the solid residue was analyzed by ^1H NMR spectroscopy (in DMSO- d_6), comparing the integral intensities of signals. The data on the product composition are given in Table 3.

12,12',12'',12'''-Cyclobutane-*r*-1,*c*-2,*t*-3,*t*-4-tetrayltetrakis-2,3,5,6,8,9-hexahydro-1,4,7,10-benzotetraoxacyclododecine *rc*tt-4a and 12,12',12'',12'''-cyclobutane-*r*-1,*t*-2,*c*-3,*t*-4-tetrayltetrakis-2,3,5,6,8,9-hexahydro-1,4,7,10-benzotetraoxacyclododecine *rt*ct-4a, complexes with $\text{Ba}(\text{ClO}_4)_2$. A solution of a mixture of (*E*)-1a (7.2 mg, 15.3 μmol) and $\text{Ba}(\text{ClO}_4)_2$ (5.6 mg, 16.8 μmol) in MeCN (15 cm^3) was irradiated for 2 h according to the above described procedure. According to ^1H NMR data, the reaction mixture consisted of *rc*tt-4a, *rt*ct-4a, and 4'-formylbenzo-12-crown-4 ether (**3a**) in 8.7 : 3.6 : 1 molar ratio; $\lambda_{\text{max}}(\text{MeCN})/\text{nm}$ 282 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 11 800); m/z (ESI MS) 495.1935 (calc. for $\text{C}_{52}\text{H}_{64}\text{O}_{16}\cdot 2\text{Na}^+$: 495.1995) and 967.4023 (calc. for $\text{C}_{52}\text{H}_{64}\text{O}_{16}\cdot \text{Na}^+$: 967.4092). *rc*tt-4a: δ_{H} (500 MHz; DMSO- d_6 ; 30 $^\circ\text{C}$) 3.54 (16 H, s, 8 \times CH_2O), 3.55 (8 H, m, 4 \times $\text{CH}_2\text{CH}_2\text{OAr}$), 3.60 (8 H, m, 4 \times $\text{CH}_2\text{CH}_2\text{OAr}$), 3.90 (8 H, m, 4 \times CH_2OAr), 3.98 (8 H, m, 4 \times CH_2OAr), 4.27 (4 H, s, 4 \times CHAr), 6.75 (4 H, d, J 1.8, 4 \times 2-H), 6.76 (4 H, dd, J 8.2 and 1.8, 4 \times 6-H) and 6.82 (4 H, d, J 8.2, 4 \times 5-H). *rt*ct-4a: δ_{H} (500 MHz; DMSO- d_6 ; 30 $^\circ\text{C}$) 3.40 (4 H, s, 4 \times CHAr), 3.61 (16 H, s, 8 \times CH_2O), 3.68 (16 H, m, 8 \times $\text{CH}_2\text{CH}_2\text{OAr}$), 4.04 (8 H, m, 4 \times CH_2OAr), 4.07 (8 H, m, 4 \times CH_2OAr), 6.91 (4 H, dd, J 8.2 and 1.8, 4 \times 6-H), 6.94 (4 H, d, J 8.2, 4 \times 5-H) and 7.01 (4 H, d, J 1.8, 4 \times 2-H).

15,15',15'',15'''-Cyclobutane-*r*-1,*c*-2,*t*-3,*t*-4-tetrayltetrakis-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine *rc*tt-4b, complex with KClO_4 . A solution of a mixture of (*E*)-1b (29.4 mg, 52.5 μmol) and KClO_4 (7.3 mg, 52.5 μmol) in MeCN (15 cm^3) was irradiated for 10 h according to the above described procedure. The reaction mixture was concentrated to a volume of $\sim 7 \text{ cm}^3$ and slowly saturated with benzene by the vapour diffusion method at ambient temperature until colourless crystals were formed. The crystals were separated by decantation and dried at 80 $^\circ\text{C}$ *in vacuo* to yield compound *rc*tt-4b (20.9 mg, 56%) as the 1 : 2 complex with KClO_4 ; mp > 310 $^\circ\text{C}$ (dec.) (Found: C, 50.58; H, 5.59. Calc. for $\text{C}_{60}\text{H}_{80}\text{O}_{20}\cdot 2\text{KClO}_4\cdot 1.5\text{H}_2\text{O}$: C, 50.56; H, 5.87%); $\lambda_{\text{max}}(\text{MeCN})/\text{nm}$ 281 and 235 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 11 400 and 26 900); δ_{H} (500 MHz; DMSO- d_6 ; 25 $^\circ\text{C}$) 3.60 (16 H, m, 8 \times CH_2O), 3.66 (24 H, m, 8 \times CH_2O and 4 \times 3- $\text{CH}_2\text{CH}_2\text{OAr}$), 3.75 (16 H, m, 4 \times 4- $\text{CH}_2\text{CH}_2\text{OAr}$ and 4 \times 3- CH_2OAr), 3.99 (8 H, m, 4 \times 4- CH_2OAr), 4.28 (4 H, s, 4 \times CHAr), 6.37 (4 H, br s, 4 \times 2-H), 6.80 (4 H, d, J 8.2, 4 \times 5-H) and 6.85 (4 H, br d, J 8.2, 4 \times 6-H); δ_{C} (125 MHz; DMSO- d_6 ; 25 $^\circ\text{C}$) 44.96

(4 \times CHAr), 66.35 (4 \times 4- CH_2OAr), 66.46 (4 \times 3- CH_2OAr), 66.77 (4 \times 3- $\text{CH}_2\text{CH}_2\text{OAr}$), 67.35 (4 \times 4- $\text{CH}_2\text{CH}_2\text{OAr}$), 67.85 (4 \times CH_2O), 68.24 (4 \times CH_2O), 68.54 (4 \times CH_2O), 68.59 (4 \times CH_2O), 111.27 (4 \times 5-C), 113.01 (4 \times 2-C), 119.91 (4 \times 6-C), 133.29 (4 \times 1-C), 145.18 (4 \times 4-C) and 146.54 (4 \times 3-C); m/z (ESI MS) 583.2481 (calc. for $\text{C}_{60}\text{H}_{80}\text{O}_{20}\cdot 2\text{Na}^+$: 583.2519), 591.2345 (calc. for $\text{C}_{60}\text{H}_{80}\text{O}_{20}\cdot \text{Na}^+\cdot \text{K}^+$: 591.2388), 599.2310 (calc. for $\text{C}_{60}\text{H}_{80}\text{O}_{20}\cdot 2\text{K}^+$: 599.2258), 1143.5127 (calc. for $\text{C}_{60}\text{H}_{80}\text{O}_{20}\cdot \text{Na}^+$: 1143.5140) and 1159.4764 (calc. for $\text{C}_{60}\text{H}_{80}\text{O}_{20}\cdot \text{K}^+$: 1159.4880).

Cyclobutane *rc*tt-4b, complex with $\text{Ca}(\text{ClO}_4)_2$. A solution of a mixture of (*E*)-1b (41.4 mg, 73.9 μmol) and $\text{Ca}(\text{ClO}_4)_2$ (19.4 mg, 81.3 μmol) in MeCN (15 cm^3) was irradiated for 5 h according to the above described procedure. The reaction mixture was concentrated to a volume of $\sim 10 \text{ cm}^3$ and slowly saturated with benzene–dioxane mixture ($\sim 2 : 1$, v/v) by the vapour diffusion method at ambient temperature until a light-beige precipitate was formed. This precipitate was recrystallized under the same conditions to give compound *rc*tt-4b (53.0 mg, 86%; impurity of *rt*ct-4b < 2 mol%) as the 1 : 2 complex with $\text{Ca}(\text{ClO}_4)_2$; mp > 270 $^\circ\text{C}$ (dec.) (Found: C, 43.30; H, 4.91. Calc. for $\text{C}_{60}\text{H}_{80}\text{O}_{20}\cdot 2\text{Ca}(\text{ClO}_4)_2\cdot 3.5\text{H}_2\text{O}$: C, 43.35; H, 5.28%); $\lambda_{\text{max}}(\text{MeCN})/\text{nm}$ 282 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 10 400); δ_{H} (500 MHz; DMSO- d_6 ; 28 $^\circ\text{C}$) 3.57 (32 H, m, 16 \times CH_2O), 3.66 (8 H, m, 4 \times 3- $\text{CH}_2\text{CH}_2\text{OAr}$), 3.70 (8 H, m, 4 \times 4- $\text{CH}_2\text{CH}_2\text{OAr}$), 3.87 (8 H, m, 4 \times 3- CH_2OAr), 3.93 (8 H, m, 4 \times 4- CH_2OAr), 4.26 (4 H, s, 4 \times CHAr), 6.69 (4 H, br s, 4 \times 2-H), 6.71 (4 H, br d, J 8.2, 4 \times 6-H) and 6.73 (4 H, d, J 8.2, 4 \times 5-H); δ_{C} (125 MHz; DMSO- d_6 ; 26 $^\circ\text{C}$) 46.31 (4 \times CHAr), 68.32 (4 \times 4- CH_2OAr), 68.44 (4 \times 3- CH_2OAr), 68.65 (4 \times 3- $\text{CH}_2\text{CH}_2\text{OAr}$), 68.81 (4 \times 4- $\text{CH}_2\text{CH}_2\text{OAr}$), 69.74 (8 \times CH_2O), 70.27 (4 \times CH_2O), 70.33 (4 \times CH_2O), 113.25 (4 \times 5-C), 114.67 (4 \times 2-C), 120.43 (4 \times 6-C), 133.78 (4 \times 1-C), 146.68 (4 \times 4-C) and 147.77 (4 \times 3-C).

Cyclobutane *rc*tt-4b. A solution of Me_4NOH (20%, aq.) (69 μcm^3 , 152.0 μmol) was added to a mixture of complex *rc*tt-4b [$\text{Ca}(\text{ClO}_4)_2$] $\cdot 3.5\text{H}_2\text{O}$ (39.3 mg, 23.6 μmol) and ethylenediaminetetraacetic acid (20.2 mg, 69.1 μmol) in water (3 cm^3). The resulting solution was thoroughly evaporated *in vacuo* at 30 $^\circ\text{C}$ and the solid residue was extracted with benzene (2 \times 20 cm^3). The extracts were evaporated *in vacuo* to yield free *rc*tt-4b (24.3 mg, 92%) as a slightly yellowish powder; mp 70–73 $^\circ\text{C}$ (Found: C, 64.23; H, 7.09. Calc. for $\text{C}_{60}\text{H}_{80}\text{O}_{20}$: C, 64.27; H, 7.19%); $\lambda_{\text{max}}(\text{MeCN})/\text{nm}$ 284 and 232 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 12 500 and 30 800); δ_{H} (500 MHz; DMSO- d_6 ; 26 $^\circ\text{C}$) 3.57 (32 H, m, 16 \times CH_2O), 3.66 (8 H, m, 4 \times 3- $\text{CH}_2\text{CH}_2\text{OAr}$), 3.70 (8 H, m, 4 \times 4- $\text{CH}_2\text{CH}_2\text{OAr}$), 3.87 (8 H, m, 4 \times 3- CH_2OAr), 3.93 (8 H, m, 4 \times 4- CH_2OAr), 4.26 (4 H, s, 4 \times CHAr), 6.69 (4 H, br s, 4 \times 2-H), 6.71 (4 H, br d, J 8.2, 4 \times 6-H) and 6.73 (4 H, d, J 8.2, 4 \times 5-H); δ_{C} (125 MHz; DMSO- d_6 ; 26 $^\circ\text{C}$) 46.31 (4 \times CHAr), 68.30 (4 \times 4- CH_2OAr), 68.44 (4 \times 3- CH_2OAr), 68.64 (4 \times 3- $\text{CH}_2\text{CH}_2\text{OAr}$), 68.79 (4 \times 4- $\text{CH}_2\text{CH}_2\text{OAr}$), 69.72 (8 \times CH_2O), 70.25 (4 \times CH_2O), 70.30 (4 \times CH_2O), 113.23 (4 \times 5-C), 114.67 (4 \times 2-C), 120.41 (4 \times 6-C), 133.75 (4 \times 1-C), 146.67 (4 \times 4-C) and 147.76 (4 \times 3-C).

18,18',18'',18'''-Cyclobutane-*r*-1,*c*-2,*t*-3,*t*-4-tetrayltetrakis-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxa-cyclooctadecine *rectt*-4c, complex with CsClO₄. A solution of a mixture of (*E*)-**1c** (20.3 mg, 31.3 μmol) and CsClO₄ (7.7 mg, 32.9 μmol) in MeCN (15 cm³) was irradiated for 3 h according to the above described procedure. The reaction mixture was concentrated to a volume of ~5 cm³ and slowly saturated with benzene by the vapour diffusion method at ambient temperature until colourless druses were formed. These druses were separated by decantation and dried at 80 °C *in vacuo* to yield compound *rectt*-**4c** (21.2 mg, 73%) as the 1 : 2 complex with CsClO₄; mp 222–224 °C (Found: C, 46.57; H, 5.61. Calc. for C₆₈H₉₆O₂₄·2CsClO₄·0.15C₆H₆: C, 46.65; H, 5.51%); λ_{max}(MeCN)/nm 281 and 235 (ε/dm³ mol⁻¹ cm⁻¹ 14 700 and 35 200); δ_H(500 MHz; DMSO-*d*₆; 30 °C) 3.55–3.62 (40 H, m, 20 × CH₂O), 3.65 (16 H, m, 8 × CH₂O), 3.68–3.78 (16 H, m, 4 × 4-CH₂CH₂OAr and 4 × 3-CH₂OAr), 4.03 (8 H, m, 4 × 4-CH₂OAr), 4.27 (4 H, s, 4 × CHAr), 6.27 (4 H, br s, 4 × 2-H), 6.84 (4 H, d, *J* 8.3, 4 × 5-H) and 6.89 (4 H, br d, *J* 8.3, 4 × 6-H); δ_C(125 MHz; DMSO-*d*₆; 26 °C) 44.37 (4 × CHAr), 66.18 (4 × 4-CH₂OAr), 66.62 (4 × 3-CH₂OAr), 67.54 (4 × CH₂O), 67.74 (4 × CH₂O), 68.46 (4 × CH₂O), 68.89 (4 × CH₂O), 69.05 (8 × CH₂O), 69.27 (4 × CH₂O), 69.55 (4 × CH₂O), 110.34 (4 × 5-C), 112.41 (4 × 2-C), 119.40 (4 × 6-C), 132.51 (4 × 1-C), 144.99 (4 × 4-C) and 146.29 (4 × 3-C); *m/z* (ESI MS) 347.1417 (calc. for C₆₈H₉₆O₂₄·4Na⁺: 347.1471), 455.1924 (calc. for C₆₈H₉₆O₂₄·3Na⁺: 455.1995), 671.2965 (calc. for C₆₈H₉₆O₂₄·2Na⁺: 671.3044) and 679.2836 (calc. for C₆₈H₉₆O₂₄·Na⁺·K⁺: 679.2913).

Cyclobutane *rectt*-4c, complex with salt C3. A solution of a mixture of (*E*)-**1c** (40.1 mg, 61.9 μmol) and 1,3-propanedi-ammonium diperchlorate (**C3**) (18.7 mg, 68.1 μmol) in MeCN (15 cm³) was irradiated for 4 h according to the above described procedure. The reaction mixture was concentrated to a volume of ~10 cm³ and slowly saturated with benzene by the vapour diffusion method at ambient temperature until a slightly yellowish amorphous precipitate was formed. This precipitate was separated by decantation and dried at 80 °C *in vacuo* to yield compound *rectt*-**4c** (42.6 mg, 75%) as the 1 : 2 complex with **C3**; mp 192–195 °C (Found: C, 48.04; H, 6.61; N, 2.95. Calc. for C₆₈H₉₆O₂₄·2C₃H₁₂Cl₂N₂O₈: C, 48.11; H, 6.55; N, 3.03%); λ_{max}(MeCN)/nm 280 and 231 (ε/dm³ mol⁻¹ cm⁻¹ 17 700 and 43 900); δ_H(500 MHz; DMSO-*d*₆; 26 °C) 1.79 (4 H, m, 2 × CH₂CH₂NH₃), 2.85 (8 H, m, 4 × CH₂NH₃), 3.51 (16 H, m, 8 × CH₂O), 3.54 (16 H, m, 8 × CH₂O), 3.57 (16 H, m, 8 × CH₂O), 3.65 (8 H, m, 4 × 3-CH₂CH₂OAr), 3.69 (8 H, m, 4 × 4-CH₂CH₂OAr), 3.91 (8 H, m, 4 × 3-CH₂OAr), 3.95 (8 H, m, 4 × 4-CH₂OAr), 4.26 (4 H, s, 4 × CHAr), 6.696 (4 H, br d, *J* 8.6, 4 × 6-H), 6.703 (4 H, br s, 4 × 2-H), 6.74 (4 H, d, *J* 8.6, 4 × 5-H) and 7.67 (12 H, br s, 4 × NH₃).

Cyclobutane *rectt*-4c. A dispersion of complex *rectt*-**4c**·(**C3**)₂ (35.1 mg, 19.0 μmol) or *rectt*-**4c**·(**C4**)₂⁹ (46.0 mg, 24.5 μmol) in water (20–30 cm³) was extracted with a mixture of benzene (25–30 cm³) and CH₂Cl₂ (10–15 cm³). The organic extract was evaporated *in vacuo* to yield free *rectt*-**4c** [15.8 mg, yield 64% in the case of *rectt*-**4c**·(**C3**)₂ or 27.7 mg, yield 87% in the case of

rectt-**4c**·(**C4**)₂] as a slightly yellowish viscous oil; λ_{max}(MeCN)/nm 283 and 232 (ε/dm³ mol⁻¹ cm⁻¹ 14 800 and 33 000); δ_H(500 MHz; DMSO-*d*₆; 26 °C) 3.52 (16 H, s, 8 × CH₂O), 3.54 (16 H, m, 8 × CH₂O), 3.58 (16 H, m, 8 × CH₂O), 3.66 (8 H, m, 4 × 3-CH₂CH₂OAr), 3.70 (8 H, m, 4 × 4-CH₂CH₂OAr), 3.91 (8 H, m, 4 × 3-CH₂OAr), 3.96 (8 H, m, 4 × 4-CH₂OAr), 4.27 (4 H, s, 4 × CHAr), 6.70 (4 H, br d, *J* 8.2, 4 × 6-H), 6.71 (4 H, br s, 4 × 2-H) and 6.75 (4 H, d, *J* 8.2, 4 × 5-H); δ_C(125 MHz; DMSO-*d*₆; 26 °C) 46.42 (4 × CHAr), 68.02 (4 × 4-CH₂OAr), 68.08 (4 × 3-CH₂OAr), 68.61 (4 × 3-CH₂CH₂OAr), 68.76 (4 × 4-CH₂CH₂OAr), 69.77 (24 × CH₂O), 112.69 (4 × 5-C), 114.06 (4 × 2-C), 120.21 (4 × 6-C), 133.60 (4 × 1-C), 146.34 (4 × 4-C) and 147.40 (4 × 3-C).

¹H NMR titration

The titration experiments were performed in MeCN-*d*₃ (the water content ≤ 0.05%, FGUP RNTs Prikladnaya Khimiya, St. Petersburg, Russian Federation) or MeCN-*d*₃-D₂O (10 : 1, v/v) solutions at 30 ± 1 °C. The concentration of (*E*)-**1a-c**, B15C5 was maintained at about (1, 2, or 5) × 10⁻³ M depending on solubility of the components and/or complexes. The concentration of metal perchlorate or **C3** in the solution was gradually increased starting from zero. The highest salt/**1**(B15C5) concentration ratios were about 3–5. The proton chemical shifts were measured as a function of the salt/**1**(B15C5) ratio. The Δδ_H values were measured with an accuracy of 0.001 ppm and then the complex formation constants were calculated using the HYPNMR program.²¹ In the case of log *K*_{1:1} > 5, the values of log *K*_{2:2} and/or log *K*_{1:2} were determined taking into account a fixed rough value for log *K*_{1:1} which was chosen by the criterion of minimal rms weighted residuals.

X-Ray crystallography

The crystals of complexes of stilbenes (*E*)-**1b,c** and cyclobutane *rectt*-**4b** were grown as described above. The single crystals of all compounds were coated with perfluorinated oil and mounted on a Bruker SMART-CCD diffractometer [graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å) or Cu-K_α radiation (λ = 1.54178 Å), ω scan mode] under a stream of cold nitrogen (*T* = 120.0(2) or 100(2) K, respectively). The sets of experimental reflections were measured and the structures were solved by direct methods and refined with anisotropic thermal parameters for all non-hydrogen atoms (except for the strongly disordered picrate anion and benzene molecule in structure **1c**·CsPic·C₆H₆ and one of independent benzene molecules in structure **1c**·**C3**·2.67C₆H₆, which were refined isotropically). In some cases, absorption correction was applied using the SADABS method. The hydrogen atoms were fixed at calculated positions at carbon atoms and then refined with an isotropic approximation for **1b**·2Ca(ClO₄)₂·2MeCN·4H₂O or using a riding model for other structures. The hydrogen atoms of the NH₃⁺ group in structure **1c**·**C3**·2.67C₆H₆ were calculated geometrically and refined using a riding model. Hydrogen atoms of the solvation water molecules in structure **1b**·2Ca(ClO₄)₂·2MeCN·4H₂O were located from the difference Fourier map and refined

isotropically. In other hydrated structures, hydrogen atoms of the water molecules were not located.

Crystal data for **1b**·2NaClO₄: C₃₀H₄₀Cl₂Na₂O₁₈, *M* = 805.50, monoclinic, *a* = 26.083(2), *b* = 9.2443(9), *c* = 15.8150(13) Å, *β* = 96.659(5)°, *V* = 3787.5(6) Å³, space group *P*2₁/*c* (no. 14), *Z* = 4, *μ* = 0.269 mm⁻¹, 45 379 reflections measured, 9987 unique (*R*_{int} = 0.5344) which were used in all calculations. The final *R*₁ and *wR*₂ were 0.2426 and 0.3541 (for 3733 reflections with *I* > 2σ(*I*)), 0.4133 and 0.4098 (for all data). The ISOR command was applied for the most non-hydrogen atoms. The experiment was collected from a weakly reflected crystal. For this reason, the final parameters are characterized by low accuracy. Unfortunately, we failed to obtain better crystals and better structural data. Nevertheless, we included this structure in this article without a discussion of thin details of the geometry just in order to show one more type of coordination mode of **1b** to a metal cation.

Crystal data for **1b**·2Ca(ClO₄)₂·2MeCN·4H₂O: C₃₄H₅₄Ca₂Cl₄N₂O₃₀, *M* = 1192.75, monoclinic, *a* = 8.1196(2), *b* = 16.2587(5), *c* = 19.1065(5) Å, *β* = 97.303(1)°, *V* = 2501.84(12) Å³, space group *P*2₁/*n* (no. 14), *Z* = 2, *μ* = 0.538 mm⁻¹, 17932 reflections measured, 6562 unique (*R*_{int} = 0.0164) which were used in all calculations. The final *R*₁ and *wR*₂ were 0.0345 and 0.0898 (for 6044 reflections with *I* > 2σ(*I*)), 0.0378 and 0.0940 (for all data). The both independent perchlorate anions are disordered over two positions with occupancies 0.62 : 0.38 and 0.70 : 0.30. The ISOR command was applied for atom O(25) of anion Cl(2)O₄⁻.

Crystal data for **1b**·KPic·C₆H₆: C₄₂H₄₈KN₃O₁₇, *M* = 905.93, triclinic, *a* = 12.3927(10), *b* = 13.7956(11), *c* = 14.7748(12) Å, *α* = 104.967(4), *β* = 108.561(4), *γ* = 105.014(4)°, *V* = 2146.7(3) Å³, space group *P* $\bar{1}$ (no. 2), *Z* = 2, *μ* = 0.203 mm⁻¹, 15 990 reflections measured, 10 796 unique (*R*_{int} = 0.0708) which were used in all calculations. The final *R*₁ and *wR*₂ were 0.1104 and 0.2224 (for 4212 reflections with *I* > 2σ(*I*)), 0.2583 and 0.2690 (for all data). The solvate benzene molecule is disordered over two positions with occupancies 0.63 : 0.37. The ISOR command was applied for all carbon atoms of the disordered benzene molecule.

Crystal data for **1c**·CsPic·C₆H₆: C₄₆H₅₆CsN₃O₁₉, *M* = 1087.85, triclinic, *a* = 12.7413(3), *b* = 17.2121(4), *c* = 23.8339(5) Å, *α* = 83.200(1), *β* = 80.486(1), *γ* = 70.437(1)°, *V* = 4846.22(19) Å³, space group *P*1 (no. 2), *Z* = 4, *μ* = 0.844 mm⁻¹, 62 607 reflections measured, 25 689 unique (*R*_{int} = 0.0774) which were used in all calculations. The final *R*₁ and *wR*₂ were 0.0808 and 0.2017 (for 11 775 reflections with *I* > 2σ(*I*)), 0.1801 and 0.2340 (for all data). Many of independent components of the crystal cell are strongly disordered (see a detailed description in the corresponding CIF file available from the CCDC) and because we needed to apply a number of the SADI, FLAT, and ISOR commands to constrain their geometric and anisotropic parameters.

Crystal data for **1c**·C₃·2.67C₆H₆: C₅₃H₇₆Cl₂N₂O₂₀, *M* = 1132.06, trigonal, *a* = *b* = 21.0741(3), *c* = 33.4590(6) Å, *V* = 12868.9(3) Å³, space group *R*32 (no. 155), *Z* = 9, *μ* = 1.659 mm⁻¹ (for Cu-K_α radiation), 14 469 reflections measured, 4708 unique (*R*_{int} = 0.0421) which were used in all calculations. The final *R*₁ and *wR*₂ were 0.0628 and 0.1753 (for 4541 reflections with *I* > 2σ(*I*)), 0.0647 and 0.1790 (for all

data). Molecule **1c** reveals a complicated disorder in crystal (see Fig. S1a, ESI[†]). Three crystallographically independent perchlorate anions are also disordered: they occupy two different positions with symmetry 3222 and special position in 2-fold axis. One solvate benzene molecule reveals rotation disorder in its plane over two positions with occupancies 0.66 : 0.34, whereas, the second benzene molecule is situated in 3-fold axis. The SADI and ISOR commands were applied to some atoms of the disordered perchlorate anions and bis(18-crown-6)stilbene molecule. In this X-ray experiment, 5 ClO₄⁻ anions per 3 propanediammonium ions have been found, although 2 anions per organic dication are required for electrical neutrality of compound **C3**. This discrepancy may only be eliminated if the formula unit H₃N⁺(CH₂)₃NH₃⁺ is partly statistically deprotonated. On the other hand, elemental analysis data for this complex agree well with complete protonation of this species (see above). We cannot explain this disagreement now. We only note that all crystal space is filled completely and no residual electron density peaks higher than 0.43 e⁻ Å⁻³ that could be assigned as the additional ClO₄⁻ anion occur.

Crystal data for *rctt*-**4b**·2KClO₄·2C₆H₆·4H₂O: C₇₂H₁₀₀Cl₂K₂O₃₂, *M* = 1626.62, monoclinic, *a* = 13.9879(9), *b* = 26.9584(19), *c* = 21.0031(15) Å, *β* = 103.011(4)°, *V* = 7716.8(9) Å³, space group *C*2/*c* (no. 15), *Z* = 4, *μ* = 0.279 mm⁻¹, 43 634 reflections measured, 10 251 unique (*R*_{int} = 0.1790) which were used in all calculations. The final *R*₁ and *wR*₂ were 0.1020 and 0.2778 (for 4619 reflections with *I* > 2σ(*I*)), 0.2154 and 0.3110 (for all data). Three of four independent solvate water molecules have incomplete position occupancies. The ISOR command was applied to 6 atoms.

Crystal data for *rctt*-**4b**·2Ca(ClO₄)₂·3C₆H₆·9H₂O: C₇₈H₁₁₆Ca₂Cl₄O₄₅, *M* = 1995.67, triclinic, *a* = 14.4368(8), *b* = 17.9290(11), *c* = 18.9170(11) Å, *α* = 78.740(3), *β* = 84.002(3), *γ* = 87.880(3)°, *V* = 4775.2(5) Å³, space group *P* $\bar{1}$ (no. 2), *Z* = 2, *μ* = 0.324 mm⁻¹, 46 792 reflections measured, 25 054 unique (*R*_{int} = 0.2700) which were used in all calculations. The final *R*₁ and *wR*₂ were 0.1145 and 0.2320 (for 5685 reflections with *I* > 2σ(*I*)), 0.3780 and 0.2961 (for all data). One of five independent perchlorate anions, Cl(3)O₄⁻, is disordered over two positions with occupancies 0.77 : 0.23. Anions Cl(4)O₄⁻ and Cl(5)O₄⁻ have occupancies of 0.61 and 0.39, respectively. Some of the eleven solvate water molecules have incomplete occupancies. The ISOR command was applied to some non-hydrogen atoms.

All the calculations were performed using the SHELXTL-Plus software.²² CCDC reference numbers 780037 (**1b**·2NaClO₄), 780035 [**1b**·2Ca(ClO₄)₂·2MeCN·4H₂O], 780036 (**1b**·KPic·C₆H₆), 780039 (**1c**·CsPic·C₆H₆), 780038 (**1c**·C₃·2.67C₆H₆), 780041 (*rctt*-**4b**·2KClO₄·2C₆H₆·4H₂O), and 780040 [*rctt*-**4b**·2Ca(ClO₄)₂·3C₆H₆·9H₂O].

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