Azidocryptands–synthesis, structure, and complexation properties†

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Cryptands bearing an intraannular azido substituent have been synthesized and characterized spectroscopically. Their complexation properties were investigated by picrate extraction analysis. The oxygen-containing cryptands were found to be good ligands for alkali cations, with a preference for Li^+ and Na^+. The molecular structure of the complex with KBr was determined by X-ray crystallography. In this, the first structurally characterized complex of an aryl azide bound to a metal cation, the potassium cation was found to show ninefold coordination to four oxygen atoms and two nitrogen atoms of the crown ether moiety, to the bromide anion and to N1 of the azido group, as well as C1 of the benzene ring.

Introduction

Ever since Pedersen's seminal work,[1] crown ethers and cryptands have been the focus of research for their remarkable selectivity in the complexation of alkali and alkaline earth cations.[2–6] In simple crown ethers and cryptands, the cations are bound to the ring heteroatoms (oxygen, nitrogen or sulfur). Intraannular functionalization of crown ethers and cryptands can be achieved by introducing a *m*-phenylene or similar aromatic linker into the ring. Intraannularly nitro-,[7–9] azo- and diazonio-,[7] and diazo-[10] functionalized cryptands and crown ethers have thus been synthesized.

Intraannular functionalization of crown ethers and cryptands can lead to significant changes in the complexation behavior of the host molecules. Generally, if Lewis-basic substituents are placed within the ring, complexation is favored. Examples include pyridine-bridged cryptands[9] and heteroaromatic *N*-oxides,[8] but also the weak Lewis-base fluorine.[11–15] Electron-deficient substituents may be stabilized in the electron-rich interior of a crown ether, as has been observed in the case of intraannular diazonium ions.[7] Steric requirements also play an important role. Depending on the ring size, intraannular nitro substitution can lead to enhanced complexation, which is due to the presence of the two nitro oxygen atoms as additional binding sites. It may, however, also lead to a decrease in complex forming constants, as the nitro group has steric requirements, that may compete with the steric requirements of the cation.[8] This study focuses on the intraannular functionalization of cryptands by another functional group; azide, $–N_3$. Aryl azides are remarkable for their fascinating photochemistry, the outcome of which strongly depends on the structure of the azide and may be influenced by a number of factors such as presence of *ortho* substituents, nearby C–H bonds or electron-donating or -withdrawing *para*-substituents. This work is in the context of a broader study designed to investigate the properties of intraannularly azido-functionalized cryptands.[16] We have used extraction analysis to study the complexation properties of a series of these ligands. The results are complemented by a study of spectroscopic properties of the azidocryptands and by the structural characterization of a number of azidocryptands and one azidocryptand–potassium bromide complex.

Results and discussion

Synthesis of azidocryptands

The azidocryptands **1–4** have been synthesized according to the synthetic procedure reported for the analogous unsubstituted system **5** and the corresponding fluoro-substituted system **6**.[12]

This procedure is based on a condensation of 1,3-bis-(bromomethyl)-2-azidobenzene and a diaza-crown ether, in the presence of a suitable alkali metal carbonate, using acetonitrile as solvent (Scheme 1).

In the case of **1**, the cryptand is obtained by performing the cyclization in presence of potassium carbonate (Table 1). Treatment of the free ligand with LiBr yields the LiBr complex. In the case of **2**, the use of Li_2CO_3 as base yields the free cryptand. If Na_2CO_3 or K_2CO_3 are used instead the corresponding NaBr or KBr complexes of **2** are obtained. The $BaBr_2$ complex is formed from the ligand upon treatment with $BaBr_2$. Cryptand **3** is obtained in the presence of K_2CO_3. In the case of the sulfur-containing cryptand **4**, the cyclization is less effective due to the poor complexing ability for alkali metal ions. Compound **4** can be synthesised together with the dimeric species $(4)_2$ if high-dilution conditions are employed and if Cs_2CO_3 is used as base. Such dimers have been previously observed by Plenio and Diodone in the case of the synthesis of fluorocryptand **6**.[12] In contrast to the sulfur cryptand **4**, in the case of the synthesis of **6** the formation of the dimer was observed when a smaller cation (Na^+) was used, whereas in presence of a larger cation (K^+) the monomeric species was obtained.

Spectroscopy

Cryptands **1–4** show a complex pattern in their ^{1}H-NMR spectra, resembling that described by Plenio and Diodone for fluorocryptands like **6**.[12] The cryptands have a mirror plane perpendicular to the aromatic ring and the protons of each methylene group are diastereotopic, resulting in spin systems of a higher order for the ether bridges. The benzylic protons appear as two doublets. Cryptands **1**, **3** and **4** may potentially exist as two different isolable conformers. The azido group can either point towards the larger $CH_2CH_2OCH_2CH_2OCH_2CH_2$ (**1**) or $CH_2CH_2SCH_2CH_2SCH_2CH_2$ (**3**, **4**) bridge, or towards the smaller $CH_2CH_2OCH_2CH_2$ (**1**, **3**) or $CH_2CH_2SCH_2CH_2$ (**4**) bridge. NMR spectroscopy was used to identify the preferential orientation of the azido group. In the case of cryptand **1** the conformation was determined from the ROESY spectrum. The NOEs observed between the benzylic protons and the NCH_2
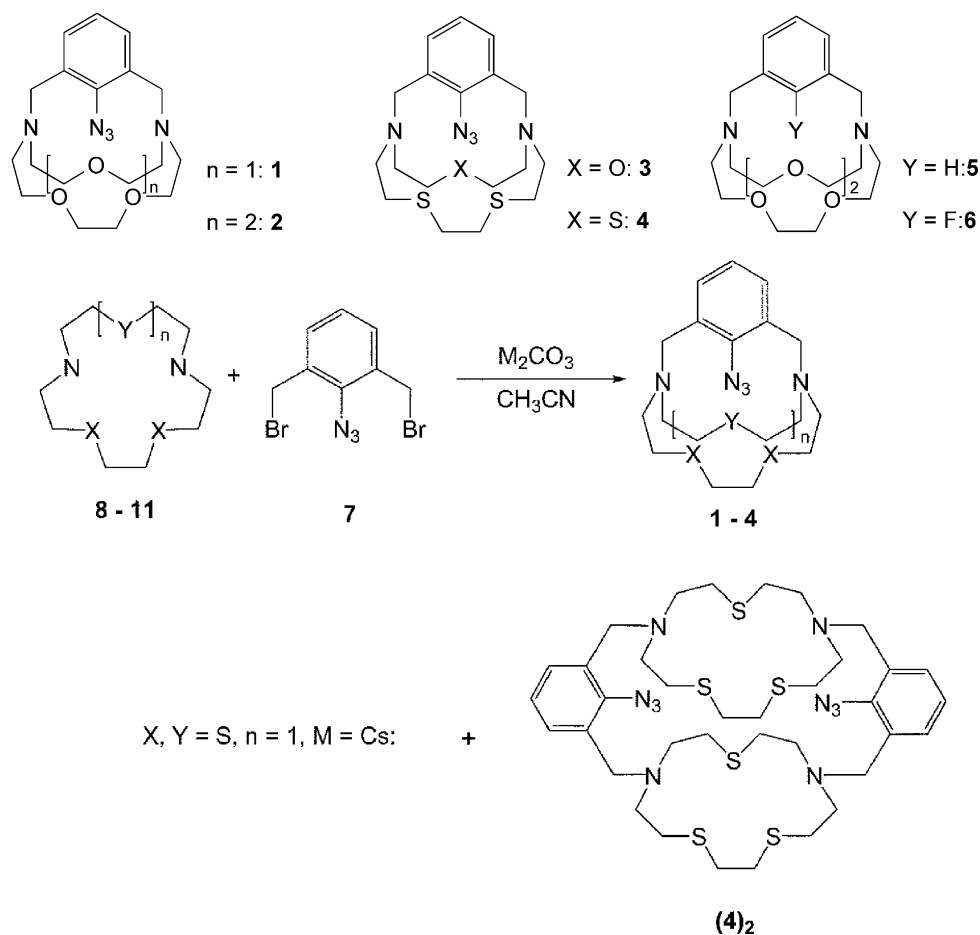
Scheme 1

Table 1 Yields of cryptands and cryptand complexes

Crown ether	Alkali carbonate	Product (yield)
8: X, Y = O; *n* = 1	K₂CO₃	**1** (24%)
9: X, Y = O; *n* = 2	Li₂CO₃	**2** (33%)
	Na₂CO₃	**2** × NaBr (24%)
	K₂CO₃	**2** × KBr (29%)
10: X = O, Y = S; *n* = 1	K₂CO₃	**3** (16%)
11: X, Y = S; *n* = 1	Cs₂CO₃	**4** + (**4**)₂ (6% + 4%)

groups of the ether chains indicate that the azido group points towards the longer chain. The shorter bridge lies above the plane of the aromatic ring so that the positions of the corresponding protons are shifted to higher fields. DFT calculations (B3LYP/6-31G(d)) support this conclusion. In the case of cryptand **1**, the stereoisomer with the azido group pointing towards the longer bridge was calculated to be more stable by 9.0 kcal mol⁻¹ than the stereoisomer with the azido group pointing towards the shorter bridge.

In the case of the sulfur-containing cryptands **3** and **4** the protons of the shorter ether bridge also show a shift to higher fields, so that it is assumed that in these systems the azido group adopts the same conformation as in cryptand **1**, namely towards the longer ether chain (CH₂CH₂SCH₂CH₂SCH₂CH₂).

In the infrared spectra, the stretching vibration of the azido group is slightly affected by cation complexation, but there is no general trend to be observed. In the uncomplexed system **2** the vibration appears at $\tilde{v}_{max}(N_3) = 2115$ cm⁻¹. In the NaBr and KBr complexes it is found at 2110 and 2108 cm⁻¹, while in the BaBr₂ complex it is shifted to 2130 cm⁻¹. For the smaller cryptand **1** very similar values are observed. In the free ligand the vibration is found at 2113 cm⁻¹ and in the LiBr complex it is shifted to 2138 cm⁻¹.

Structure

The potassium bromide complex **2** × KBr and the uncomplexed cryptands **1**, **2**, **3** and (**4**)₂ could be characterized by X-ray crystallography. The molecular structure of **2** × KBr is shown in Fig. 1 and Fig. 2 shows the structure of the corresponding free ligand **2**.
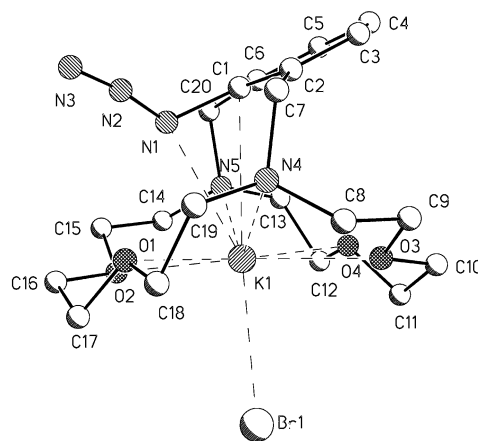

Fig. 1 Ball-and-stick plots of the molecular structure of **2** × KBr. For clarity, the hydrogen atoms have been omitted.

The potassium is coordinated to the four oxygen atoms and to the two benzylic nitrogen atoms of the ligand and appears also to be coordinated to the bromide ion, with a K–Br bond of 2.98(1) Å. In addition, N1 of the azido group and C1 of the arene chromophore also serve as coordinating sites (N1–K = 2.806(8) Å, C1–K = 3.080(8) Å). The C1–K distance indicates that, compared to the silver(I) complex **6** × AgOSO₂CF₃ (Table 2),
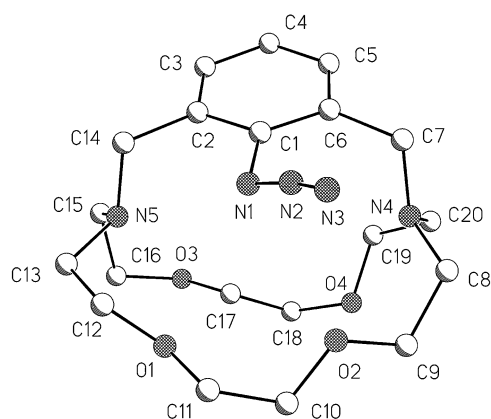
Fig. 2 Ball-and-stick plots of the molecular structure of azidocryptand **2**. For clarity, the hydrogen atoms have been omitted.

the degree of cation–π interaction is smaller in **2** × KBr. The sum of the ionic radii of K and Br is 3.29 Å (octahedral coordination), so that the K–Br distance in this [K–Br–L] complex is certainly short enough to indicate a significant bond. The benzylic nitrogen donors of the complex are bent away from the site of coordination of the bromide ion, with an N–K–N angle of 125.1(3)°. This angle is larger than the N–Ba–N angle observed in the case of **6** × Ba(ClO$_4$)$_2$[15] or the N–Na–N angle measured for **6** × NaOSO$_2$CF$_3$,[17] but is smaller than N–Ag–N in **6** × AgOSO$_2$CF$_3$ (Table 2).[13]

The interest in the structure of the potassium complex lies in the presence of the azido group. A search of the November 2003 release of the Cambridge Structural Database for structures containing an aryl azide coordinating to a metal center revealed no entries. A recent study on potassium-18-crown-6 salts of azidobenzenesulfonates and pentazolobenzenesulfonates found no evidence for an interaction of the azido groups with the potassium cation.[18a] A comparison with the structure of the uncomplexed ligands **2**, **3** and **1** with published structures of aryl azides, such as 2-(bromomethyl)azidobenzene **12**[18b] or 2,4,6-tris-*tert*-butylazidobenzene **13**[19] (two molecules in unit cell), shows that the structures are similar (Table 2). A small, but significant difference is found in the N2–N3 distance, which is shorter in **2** × KBr than in the uncomplexed azides. This may indicate a greater contribution of mesomeric structure B in **2** × KBr due to potassium complexation, for which a maximum negative charge density at N1 is required. The results of our calculations

(B3LYP/6-31G(d)) are consistent with this interpretation, as the electron density is predicted to shift slightly towards N1 upon complexation (atomic charges: N1: **2** = −0.45; **2** × K$^+$ = −0.47; N3: **2** = −0.26; **2** × K$^+$ = −0.22).
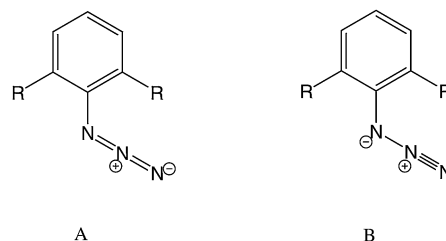
As with 2,4,6-tris-*tert*-butylazidobenzene **13**,[19] but unlike less crowded aryl azides such as **12**,[18b] the azido functionality is tilted out of the aromatic plane in **2** × KBr, **2**, **1**, and **3**. This is due to the presence of two sterically demanding *ortho* substituents in the cryptands. The results of our calculations are consistent with this observation. The calculated dihedrals C2–C1–N1–N3 are of the order of 128° to 143°.

Complexation behavior

The efficiency and selectivity of the azidocryptands in alkali metal ion complexation was studied by picrate extraction experiments. One equivalent of an aqueous solution (3 mM) of the alkali metal picrate was extracted with one equivalent of a solution of the cryptand in CH$_2$Cl$_2$ (3 mM). The amount of picrate transferred to the organic phase was determined by UV/Vis-spectroscopy. Because such picrate extraction experiments are strongly dependent on the conditions, the unsubstituted phenylcryptand **5** was also studied for comparison. Table 3 shows the extractability defined as the percent picrate extracted into the organic phase.

Extraction experiments were also performed with the sulfur containing cryptands **3** and **4**. The extractablities for alkali metal cations were ≤2% in all cases. As expected, these systems are not suitable for the complexation of alkali cations.

In the case of the unsubstituted system **5**, the extractability decreases in the order K$^+$ > Na$^+$ > Li$^+$. This series has been previously observed by Plenio *et al.* (log K_{ass} = 7.00, 6.78, 5.39).[12] They also studied the fluoro-substituted system **6** which shows the same order (log K_{ass} = 7.81, 7.67, 5.89) but the values of the association constants are larger for all three cations compared to those of the unsubstituted system **5**.

Table 2 Comparison of bond parameters of **2** × KBr, **1**, **2**, **3**, and (**4**)$_2$ with bond parameters of selected reference compounds, also with the calculated geometries of **2** × K$^+$ and **2**, as well as **1** × Na$^+$, **1** × Li$^+$ and **1**

Compound	R(N$_1$N$_2$)^a	R(N$_2$N$_3$)^a	A(N$_1$N$_2$N$_3$)^b	A(NMN)^{bc}	R(XM)^{cd}	R(C$_1$M)^c
6 × Ba(ClO$_4$)$_2$	—	—	—	116.0	2.687	3.300
6 × NaOSO$_2$CF$_3$	—	—	—	116.9	2.671	3.220
6 × AgOSO$_2$CF$_3$	—	—	—	135.9	2.714	2.830
12	1.230	1.125	172.5	—	—	—
13	1.210	1.135	172.7	—	—	—
	1.250	1.150	171.3			
2 × KBr (exp.)	1.229(8)	1.108(8)	171.0(1)	125.1(3)	2.806(8)	3.080(8)
2 × K$^+$ (calc.)	1.230	1.140	171.0	122.9	2.908	3.190
2 (exp.)	1.220	1.131	171.5	—	—	—
2 (calc.)	1.235	1.140	171.6	—	—	—
1 × Na$^+$ (calc.)^e	1.240	1.130	172.5	138.7	2.356	2.640
1 × Li$^+$ (calc.)^e	1.240	1.130	172.8	134.6	2.103	2.640
1^e (exp.)	1.231	1.130	171.4	—	—	—
1^e (calc.)	1.223	1.140	169.7	—	—	—
3 (exp.)	1.220	1.137	172.4	—	—	—
(**4**)$_2$ (exp.)	1.243	1.110	172.2	—	—	—
	1.210	1.120	169.4			

^{a} Bond lengths R in Å. ^{b} Bond angles A in °. ^{c} M = metal ion (K$^+$, Na$^+$, Ba^{2+} or Ag$^+$). ^{d} X = heteroatom bonded to C$_1$ (N or F). ^{e} Azido group pointing towards larger bridge.

Table 3 Extractability of metal picrates

	Extractability (%)		
	2	**1**	**5**
Li$^+$	24	81	22
Na$^+$	92	14	44
K$^+$	72	12	60
Rb$^+$	36	13	51
Cs$^+$	33	14	47

The extraction constants show that the azidocryptand **2** is a very good ligand for the complexation of Na$^+$ cations. K$^+$ ions are also complexed in high yield, which indicates that the cryptand is not very selective. For these two cations the azidocryptand shows a higher affinity than the unsubstituted cryptand **5**. The azido group is likely to serve as an additional donor atom and takes part in complexation. In contrast, for the larger cations Rb$^+$ and Cs$^+$ the unsubstituted system **5** is a better ligand. In this case the steric influence of the azido group prevents an effective complexation.

The smaller azidocryptand **1** shows a large extractability of Li$^+$ cations whereas the other cations are complexed to a small extent only. As the values for Na$^+$, K$^+$, Rb$^+$ and Cs$^+$ are very similar, it is very likely that the Li$^+$ cations fit exactly into the cavity, whereas the other cations are too large.

Conclusions

Cryptands bearing an intraannular azido substituent are good ligands for alkali and alkaline earth cations, if the crown ether moiety is oxocyclic. An X-ray crystallographic structure determination of a representative complex shows that N1 of the azido group serves as a coordinating site for the potassium ion, which makes it likely that it will also serve as a coordinating site in a nitrene complex generated by dediazotation of the azide. Laser flash photolysis studies indicate that this is indeed the case. The results of these studies will be published separately.

As expected, the sulfur-containing ligands **3** and **4** show little affinity towards alkali cations. These cryptands should be good ligands for late transition metal ions. We intend to study the photochemical behavior of these complexes.

Experimental

General

The synthesis of **1** has been described previously.[16]

Synthesis of the LiBr complex 1 × LiBr

Azidocryptand **1** (0.1 g, 0.28 mmol) and 0.25 g of LiBr in 30 ml of methanol were stirred for 14 h in the dark. After evaporation of the solvent, the residue was extracted with CH$_2$Cl$_2$ and excess LiBr was filtered off. The solvent was removed and the residue was again extracted with CH$_2$Cl$_2$. The whole procedure was repeated three times. Finally the LiBr complex of **1** was obtained as colorless crystals. Yield: 70 mg (0.17 mmol; 60%). Mp 141 °C (decomposition). ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 2.19–2.30 (m, 2 H), 2.40–2.50 (m, 4 H), 2.84–2.90 (m, 2 H), 3.00–3.06 (m, 2 H), 3.16–3.21 (m, 2 H), 3.51 (d, 2 H, J = 13.04 Hz, ArCH$_2$), 3.62–3.67 (m, 2 H), 3.78–3.83 (m, 6 H), 4.21 (d, 2 H, J = 13.04 Hz, ArCH$_2$), 7.22–7.29 (m, 3 H). ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$): δ = 51.49, 56.47, 59.51, 67.07, 68.55, 69.32, 127.52, 131.00, 136.91, 138.57. IR (KBr): $\tilde{v}_{max}$ = 3419 (m), 2941 (s), 2869 (s), 2138 (vs), 1588 (m), 1454 (s), 1361 (s), 1290 (s), 1087 (vs), 1008 (s), 993 (s), 930 (s), 830 (s), 776 (s), 703 (m), 636 (m) cm^{-1}. MS (FAB): m/z (%) = 368.2 (40, azidocryptand + Li$^+$), 340.2 (100, azidocryptand + Li$^+$ − N$_2$), 310.1 (5), 282.1 (7), 252 (4), 207 (4), 179.1 (5), 147.0 (5), 135.1 (8), 124.1 (5), 91.0 (5), 73.0 (10), 43.0 (10). C$_{18}$H$_{27}$O$_3$N$_5$LiBr (448.25): calcd. C 48.23, H 6.07, N 15.62; found C 48.22, H 6.26, N 15.42%.

Synthesis of 2

A mixture of 1.31 g (5 mmol) of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane and 3 g of Li$_2$CO$_3$ in 450 ml of acetonitrile was brought to reflux. A solution of 1.52 g (5 mmol) of 1-azido-2,6-bis(bromomethyl)benzene **3**[20] in 50 ml of CH$_3$CN was then added dropwise within 2 h. The mixture was refluxed for a further 16 h. The yellow solution obtained by filtration was evaporated to dryness. The yellow residue was taken up in CH$_2$Cl$_2$ and dried over MgSO$_4$. After column chromatograhic work-up (silica gel, cyclohexane : diethylamine, 9.5 : 0.5) and crystallization from pentane colorless crystals were obtained. Yield: 0.55 g (27%). Mp 156–158 °C. ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$): δ = 2.45–2.52 (m, 2 H), 2.61–2.68 (m, 2 H), 2.77–2.83 (m, 2 H), 2.92–3.00 (m, 4 H), 3.06–3.16 (m, 4 H), 3.23 (d, 2 H, J = 13.56 Hz), 3.34–3.40 (m, 2 H), 3.50–3.61 (m, 4 H), 3.70–3.78 (m, 4 H), 4.17 (d, 2 H, J = 13.56 Hz), 7.00 (t, 1 H), 7.08 (d, 2 H). ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$): δ = 55.13, 56.86, 58.11, 69.84, 70.20, 70.88, 71.67, 123.96, 130.07, 136.37, 139.86. IR (KBr): $\tilde{v}_{max}$ = 2959 (w), 2942 (w), 2878 (s), 2852 (s), 2115 (s), 1586 (m), 1471 (m), 1450 (m), 1358 (m), 1346 (m), 1321 (m), 1288 (m), 1271 (w), 1255 (w), 1242 (w), 1167 (w), 1150 (m), 1133 (m), 1113 (s), 1083 (m), 1064 (m), 1036 (w), 981 (m), 941 (m), 926 (m), 883 (w), 836 (w), 827 (w), 776 (m), 640 (w). MS (FAB): m/z (%) = 428.2 (M$^+$ + Na, 25), 406.3 (M$^+$ + H, 100), 376 (25), 362.2 (8), 288.2 (12), 275.1 (6), 259.1 (6), 245.1 (5), 233.1 (5), 203.1 (6), 187.0 (8), 172.1 (12), 159.1 (17), 144.1 (25), 130.1 (22), 118.1 (17), 104 (6), 91.0 (12), 70.1 (11), 56.0 (26), 45.0 (15). C$_{20}$H$_{31}$N$_5$O$_4$ (405.5): calcd. C 59.24, H 7.71, N 17.27; found C 59.22, H 7.90, N 17.35%.

Synthesis of the NaBr complex 2 × NaBr

The synthesis of **2** × NaBr was performed analogously to **2**. Na$_2$CO$_3$ was used instead of Li$_2$CO$_3$. Column chromatographic work-up (silica gel; CH$_2$Cl$_2$: MeOH, 9 : 1) followed by crystallization from THF–*tert*-butyl-methyl ether yielded colorless crystals. Yield: 0.3 g (24%). Mp 169 °C (decomposition). ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$): δ = 2.43–2.47 (m, 2 H), 2.68–2.75 (m, 2 H), 2.78–2.83 (m, 2 H), 2.94–3.01 (m, 2 H), 3.13–3.17 (m, 4 H), 3.25 (d, 2 H, J = 13.5 Hz), 3.42–3.46 (m, 2 H), 3.56–3.60 (m, 2 H), 3.63–3.73 (m, 4 H), 3.81–3.93 (m, 4 H), 4.07 (d, 2 H, J = 13.5 Hz), 7.25–7.31 (m, 3 H). ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$): δ = 54.38, 54.71, 57.93, 67.34, 68.53, 69.37, 69.73, 127.38, 131.16, 136.46. IR (KBr): $\tilde{v}_{max}$ = 3363 (s), 2964 (s), 2901 (s), 2879 (s), 2110 (vs), 1637 (m), 1605 (m), 1471 (m), 1452 (s), 1379 (m), 1351 (m), 1319 (m), 1293 (m), 1266 (m), 1237 (m), 1166 (m), 1103 (s), 1060 (s), 1035 (m), 1006 (m), 981 (m), 930 (m), 826 (m), 781 (m), 698 (m) cm^{-1}. MS (FAB): m/z (%) = 428.3 (20, M$^+$), 406.3 (100, M$^+$ − N$_2$), 378.3 (32), 362.3 (5), 288.2 (12), 259.2 (5), 233.2 (5), 201.1 (5), 187.1 (7), 159.1 (18), 145.1 (25), 132.3 (30), 118.1 (25), 91.1 (18), 73.1 (25), 56.1 (32), 45.0 (20). C$_{20}$H$_{31}$BrNaN$_5$O$_4$ (524.5): calcd. C 47.28, H 6.10, N 13.77; found C 47.01, H 6.09, N 13.63%.

Synthesis of the KBr complex 2 × KBr

The synthesis of **2** × KBr was performed analogously to **2**. K$_2$CO$_3$ was used instead of Li$_2$CO$_3$. Column chromatographic work-up (silica gel; CH$_2$Cl$_2$: MeOH, 9 : 1) followed by crystallization from THF–*tert*-butyl-methyl ether yielded colorless crystals. Yield: 0.75 g (29%). Mp 189 °C (decomposition). ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$): δ = 2.43–2.47 (m, 2 H), 2.68–2.72 (m, 2 H), 2.78–2.83 (m, 2 H), 2.94–3.01 (m, 2 H), 3.12–3.18 (m, 4 H), 3.26 (d, 2 H, J = 13.6 Hz), 3.41–3.46 (m, 2 H), 3.56–3.60 (m, 2 H), 3.63–3.73 (m, 4 H), 3.81–3.87 (m, 2 H), 3.88–3.93 (m, 2 H), 4.06 (d, 2 H, J = 13.6 Hz), 7.28–7.31 (m, 3 H). ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$): δ = 54.36, 54.71, 57.89, 67.30, 68.49, 69.31, 69.71, 127.32, 131.10, 136.44. IR (KBr): $\tilde{v}_{max}$ = 3574 (m), 3479 (m), 3357 (m), 2963 (m), 2901 (m), 2879 (m), 2841 (m), 2108 (s), 1637 (m), 1605 (m), 1470 (m), 1452 (m), 1379 (m), 1360 (m),

1351 (m), 1319 (m), 1293 (m), 1265 (m), 1238 (m), 1166 (m), 1127 (s), 1104 (s), 1060 (m), 1035 (m), 980 (w), 930 (m), 825 (m), 781 (m), 698 (m), 669 (m) cm^{-1}. MS (FAB): m/z (%) = 444.1 (10, M$^+$), 428.2 (100, azidocryptand + Na$^+$), 416.1 (5, M$^+$ − N$_2$), 400.2 (75, azidocryptand + Na$^+$ − N$_2$), 370.1 (5), 281.1 (5), 176.0 (5), 38.9 (12). C$_{20}$H$_{31}$BrKN$_5$O$_4$ (524.5): calcd. C 45.84, H 5.90, N 13.35; found C 45.79, H 5.87, N 13.33%.

Synthesis of the BaBr$_2$ complex 2 × BaBr$_2$

Azidocryptand **2** (0.2 g, 0.5 mmol) and 0.16 g of BaBr$_2$ × 2 H$_2$O were dissolved in a mixture of 10 ml of CH$_3$CN, 10 ml of CH$_2$Cl$_2$ and 0.1 ml of Et$_3$N and stirred for 24 h in the dark. After drying over MgSO$_4$ the solvent was removed. The product was extracted with CH$_2$Cl$_2$ and inorganic salts were separated by filtration. Crystallization from CH$_2$Cl$_2$–pentane yielded a colorless solid. Yield: 0.18 g (0.25 mmol, 50%). Mp: 188 °C (decomposition). ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$): δ = 2.56–2.59 (m, 2 H), 2.72–2.77 (m, 2 H), 3.00–3.05 (m, 2 H), 3.32–3.37 (m, 2 H), 3.51–3.57 (m, 4 H), 3.62–3.67 (m, 2 H), 3.70–3.76 (m, 4 H), 3.88–3.93 (m, 2 H), 3.97–4.04 (m, 2 H), 4.19–4.22 (m, 4 H), 4.35–4.40 (m, 2 H), 7.28 (t, J = 8 Hz, 1 H), 7.42 (d, J = 8 Hz, 2 H). ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$): δ = 59.06, 59.11, 60.43, 68.76, 69.47, 69.91, 70.02, 127.94, 130.68, 136.48, 136.62. IR (KBr): $\tilde{\nu}_{max}$ = 2914 (m), 2882 (m), 2130 (vs), 1624 (m), 1584 (m), 1477 (s), 1457 (s), 1359 (s), 1346 (m), 1327 (m), 1298 (m), 1270 (s), 1253 (m), 1241 (m), 1228 (m), 1166 (m), 1104 (s), 1067 (s), 1038 (m), 1002 (m), 986 (m), 966 (m), 935 (s), 892 (m), 861 (m), 828 (m), 811 (m), 780 (m) cm^{-1}. MS (FAB): m/z (%) 622.1 (72, azidocryptand + Ba^{2+} + Br$^-$), 594.1 (35, azidocryptand + Ba^{2+} + Br$^-$ − N$_2$), 514.2 (8), 428.2 (65, azidocryptand + Na$^+$), 400.2 (22, azidocryptand + Na$^+$ − N$_2$), 369.9 (5), 307.1 (20), 259.1 (12), 216.9 (10), 176.0 (15), 154.0 (100), 136.0 (68), 107.0 (22), 89.0 (20). C$_{20}$H$_{31}$N$_5$O$_4$BaBr$_2$ (702.6): calcd. C 34.18, H 4.45, N 9.97; found C 33.45, H 4.68, N 9.70%.

Synthesis of 3

1-Oxa-7,10-dithia-4,13-diazacyclopentadecane (0.75 g, 3 mmol) and 4 g of K$_2$CO$_3$ in 500 ml of CH$_3$CN were heated at reflux. A solution of 0.92 g (3 mmol) of 1-azido-2,6-bis(bromomethyl)benzene in 50 ml of CH$_3$CN was added during a period of 1 h. The mixture was refluxed for 18 h. The mixture was filtrated and the solvent evaporated. The residue was dissolved in CH$_2$Cl$_2$ and dried with MgSO$_4$. Purification was achieved by silica gel column chromatography with cyclohexane–diethylamine (95 : 5) and recrystallization from CH$_2$Cl$_2$–pentane. Yield: 0.18 g (15%). ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$): δ = 2.20–2.25 (m, 2 H), 2.39–2.45 (m, 2 H), 2.62–2.66 (m, 2 H), 2.71–2.81 (m, 6 H), 2.89–2.92 (m, 2 H), 3.11–3.17 (m, 4 H), 3.25 (d, 2 H, J = 12.5 Hz, ArCH_2), 3.35–3.37 (m, 2 H), 4.14 (d, 2 H, J = 12.5 Hz, ArCH_2), 6.75 (t, 1 H), 7.06 (d, 2 H). ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$): δ = 34.72, 36.69, 55.02, 60.23, 64.07, 69.97, 123.73, 131.13, 135.15, 141.83. IR (KBr): $\tilde{\nu}_{max}$ = 2957 (s), 2934 (s), 2915 (s), 2872 (s), 2839 (s), 2822 (s), 2794 (s), 2107 (vs), 1592 (m), 1468 (m), 1450 (s), 1440 (s), 1428 (m), 1370 (m), 1358 (m), 1345 (m), 1325 (m), 1308 (s), 1266 (m), 1238 (m), 1194 (m), 1145 (m), 1131 (s), 1104 (m), 1074 (m), 1057 (m), 1044 (m), 1026 (m), 1012 (m), 994 (m), 964 (m), 951 (m), 831 (m), 812 (m), 793 (m), 764 (s), 715 (m), 661 (m), 634 (m) cm^{-1}. MS (EI): m/z (%) 393 (0.5, M$^+$), 365 (10, M$^+$ − N$_2$), 350 (5), 320 (10), 306 (25), 292 (8), 272 (6), 258 (18), 230 (10), 218 (18), 205 (22), 189 (18), 172 (22), 159 (25), 132 (40), 118 (25), 100 (15), 88 (30), 70 (18), 61 (35), 56 (61), 42 (48), 28 (100). C$_{18}$H$_{27}$N$_5$S$_2$O (393.5): calcd. C 55.01, H 6.92, N 17.82, S 16.31; found C 54.94, H 7.23, N 17.84, S 16.29%.

Synthesis of 4

1,4,10-Trithia-7,13-diazacyclopentadecane (0.79 g, 3 mmol) and 9.2 g of Cs$_2$CO$_3$ in 700 ml of CH$_3$CN were heated at reflux. A solution of 0.92 g (3 mmol) of 1-azido-2,6-

bis(bromomethyl)benzene in 50 ml of CH$_3$CN was added during a period of 1 h. The mixture was refluxed for 18 h. The mixture was filtrated and the solvent evaporated. The residue was dissolved in CH$_2$Cl$_2$ and dried with MgSO$_4$. After purification by silica gel column chromatography with cyclohexane–diethylamine (95 : 5) the cryptand **4** (R_f = 0.51) and the dimer **4$_2$** (R_f = 0.26) were isolated. Yield: 0.07 g (6%) of **4** and 0.1 g (4%) of **4$_2$**. Monomer **4** ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$): δ = 1.17–1.80 (m, 2 H), 2.29–2.35 (m, 4 H), 2.51–2.71 (m, 6 H), 2.78–3.02 (m, 6 H), 3.15 (d, 2 H, J = 12.7 Hz, ArCH_2), 3.50–3.58 (m, 2 H), 4.20 (d, 2 H, J = 12.7 Hz, ArCH_2), 6.99–7.16 (m, 3 H). ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$): δ = 31.8, 35.7, 37.9, 55.4, 61.2, 62.4, 125.2, 132.8, 135.5, 141.9. IR (KBr): $\tilde{\nu}_{max}$ = 2929 (m), 2909 (s), 2870 (m), 2798 (s), 2759 (s), 2117 (vs), 1589 (m), 1465 (m), 1449 (s), 1436 (s), 1402 (m), 1370 (m), 1357 (m), 1330 (s), 1304 (s), 1262 (m), 1236 (m), 1225 (m), 1197 (m), 1182 (m), 1107 (s), 1094 (s), 1074 (m), 1022 (m), 980 (m), 968 (m), 937 (m), 923 (m), 880 (m), 800 (m), 764 (s), 730 (m), 710 (m), 632 (m). MS (EI): m/z (%) 409 (5, M$^+$), 381 (21, M$^+$ − N$_2$), 367 (15), 350 (10), 320 (15), 308 (22), 289 (5), 260 (6), 232 (10), 219 (42), 205 (35), 192 (38), 173 (36), 159 (40), 145 (60), 131 (72), 102 (50), 88 (100), 75 (35), 61 (70), 56 (55), 42 (65), 28 (90). C$_{18}$H$_{27}$N$_5$S$_3$ (409.6) calcd. C 52.78, H 6.64, N 17.10, S 23.48; found C 53.08, H 6.85, N 16.55, S 23.07%. Dimer **4$_2$**: ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$): δ = 2.30 (t, 8 H), 2.53 (t, 8 H), 2.81 (s, 8 H), 2.85–2.89 (m, 8 H), 2.93–2.96 (m, 8 H), 3.64 (s, 8 H), 7.09–7.12 (m, 6 H). ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$): δ = 28.63, 32.70, 32.85, 53.62, 56.75, 57.54, 125.46, 131.07, 135.56, 140.19. IR (KBr): $\tilde{\nu}_{max}$ = 2926 (m), 2802 (s), 2727 (m), 2439 (m), 2127 (vs), 1454 (s), 1370 (m), 1296 (m), 1267 (m), 1245 (m), 1194 (m), 1114 (m), 1095 (m), 1075 (m), 1034 (m), 914 (m), 785 (s), 735 (m), 692 (m), 631 (m) cm^{-1}. MS (FAB): m/z (%) 841.1 (0.2, M + Na$^+$), 819.2 (20, M + H$^+$), 793.2 (2), 613.1 (2), 541.1 (5), 491.1 (2), 397.1 (12), 329.0 (4), 307.1 (16), 257.0 (5), 235.0 (51), 191.0 (8), 163.0 (100), 91.0 (71).

X-Ray structure determination

The intensities were measured with a Bruker-axs-SMART diffractometer (Mo$_{K\alpha}$ radiation, λ = 0.7170 Å, ω scan) at −70 °C. The structure was solved by direct methods (SHELXS 97). Refinements were carried out with the SHELXL-97 package. All nonhydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions and refined isotropically in riding mode (C–H = 98 pm, U$_{iso}$(H) = 1.3 U$_{iso}$(C)). All refinements were made by full-matrix least-squares on F^2.

1: (C$_{18}$H$_{27}$N$_5$O$_3$): monoclinic, $P2_1/n$, a = 8.324(4) Å, b = 17.781(9) Å, c = 13.033(5) Å, β = 103.797(13)°, V = 1873.1(15) Å^3, Z = 4, μ = 0.090 mm^{-1}, 6912 measured reflections ($2\theta_{max}$ = 50°), 2857 independent reflections with 1663 observed reflections [$F_o > 4\sigma(Fo)$]. $R1[Fo > 4\sigma(Fo)]$ = 0.0706, $wR2$ [all data] = 0.1860.

2: (C$_{20}$H$_{32}$N$_5$O$_4$): monoclinic, $P2_1/n$, a = 9.572(2) Å, b = 23.209(5) Å, c = 10.117(2) Å, β = 112.214(4)°, V = 2080.7(8) Å^3, Z = 4, μ = 0.092 mm^{-1}, 7852 measured reflections ($2\theta_{max}$ = 50°), 1958 independent reflections with 3021 observed reflections [$F_o > 4\sigma(F_o)$]. $R1[F_o > 4\sigma(F_o)]$ = 0.0538, $wR2$ [all data] = 0.1216.

2 × KBr: (C$_{20}$H$_{31}$BrKN$_5$O$_4$): orthorhombic, $P2_12_12_1$, a = 10.70(4) Å, b = 13.81(5) Å, c = 15.55(6) Å, V = 2298(14) Å^3, Z = 4, μ = 2.006 mm^{-1}, 11794 measured reflections ($2\theta_{max}$ = 50°), 4099 independent reflections with 3021 observed reflections [$F_o > 4\sigma(F_o)$]. $R1[F_o > 4\sigma(F_o)]$ = 0.0584, $wR2$ [all data] = 0.1558.

3: (C$_{18}$H$_{28}$N$_5$OS$_2$): triclinic, P-1, a = 8.321(7) Å, b = 9.079(7) Å, c = 14.321(12) Å, a = 101.75(2)°, β = 101.706(16)°, γ = 103.15(2)°, V = 995.5(14) Å^3, Z = 2, μ = 0.285 mm^{-1}, 3575 measured reflections ($2\theta_{max}$ = 50°), 2649 independent reflections with 2088 observed reflections [$F_o > 4\sigma(F_o)$]. $R1[F_o > 4\sigma(F_o)]$ = 0.0503, $wR2$ [all data] = 0.1375.

(4)$_2$: (C$_{36}$H$_{56}$N$_{10}$S$_6$): monoclinic, $P2_1/n$, a = 12.683(6) Å, b = 14.165(6) Å, c = 23.626(10) Å, β = 98.430(10)° V = 4199(3)

Calculations

All calculations were performed using the *GAUSSIAN 98* suite of programs.[21] The B3LYP hybrid functional[22,23] in connection with a 6-31G(d) basis was employed for geometry optimizations and calculations of IR spectra. The calculated energies include a zero-point vibrational energy correction and refer to a temperature of 0 K.

Acknowledgements

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