

A Prime Example of Hard-Hard and Soft-Soft Interactions: Complexes between 4,7-Dioxa-1,10-diazabicyclo[8.6.6]docosa-13,19-diyne and Li^+ , Na^+ , Cu^+ , Ag^+ , Cd^{2+} , Hg^{2+}

Andreas Kunze,^[a,b] Rolf Gleiter,^{*[a]} and Frank Rominger^[a]

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The crystal structures of 4,7-dioxa-1,10-diazabicyclo[8.6.6]docosa-13,19-diyne (**7**), its *N,N'*-dioxide derivative **10** and the complexes of **7** with LiClO_4 , NaNO_3 , Cu^+ and Ag^+ triflate, $\text{Cd}(\text{NO}_3)_2$, and HgCl_2 were investigated. The Li^+ and Na^+ ions reveal a strong interaction between the ether bridge and the nitrogen atoms of **7**. The Cu^+ ion prefers an interaction between the nitrogen centers and the alkyne units whereas

the Ag^+ ion interacts with the hard oxygen and nitrogen centers as well as with the alkyne units. The reaction of HgCl_2 with **7** in the presence of water afforded a molecule which could be looked at as the intermediate of a mercury-catalyzed addition of water to the triple bonds.

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Introduction

Some time ago we found that 1,8-diazabicyclo[6.6.6]eicosa-4,11,17-triyne (**1**) provided a flexible cage structure with the *in/in* conformation of the bridgehead lone-pairs.^[1] This and the triple bonds in the bridges were responsible for including copper(I) and silver(I) ions inside the cage.^[1b] In the preceding paper we reported the synthesis and properties of diazacyptands which can be derived from **1** by replacing one 3-hexyne unit of the bridge by a tether with thioether functions (see Figure 1), the cage systems **2–6**.^[2]

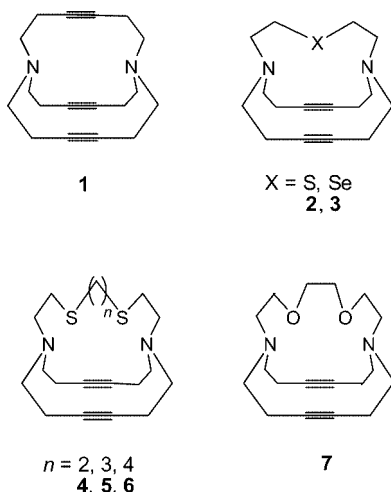


Figure 1. Bicyclic cryptands **1–7**.

[a] Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld, 270, 69120 Heidelberg, Germany
Fax: +49-6221-544205
E-mail: Rolf.Gleiter@urz.uni-heidelberg.de

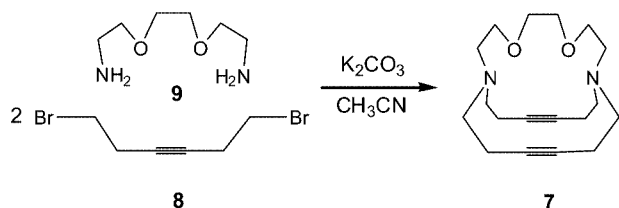
[b] CarboGen AG
Schachenallee 29, 5001 Aarau, Switzerland

The investigations of **2–6** afforded a series of endohedral copper(I) and silver(I) complexes when the reaction was carried out with copper(I) and silver(I) triflates. In the resulting complexes the soft metal ion interacted with the soft alkyne and chalcogen units as well as with the nitrogen centers. A comparison among the cryptands **2–6** revealed that the geometrical requirements for a metal heteroatom and metal-alkyne interaction were optimal in **4**. These results led us to synthesize the title compound **7** as a cryptand, because the compound should be able to host soft as well as hard ions according to the HSAB concept.^[3,4]

Results

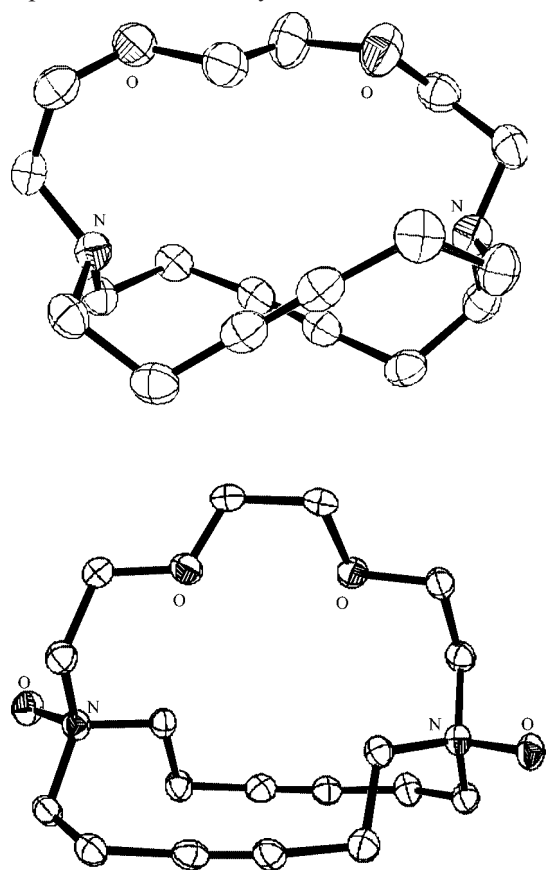
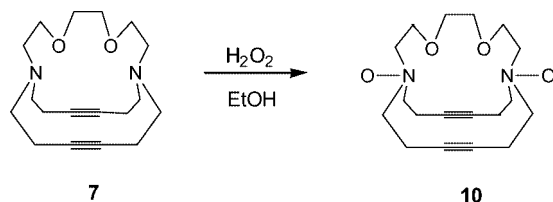
The synthesis of **7** was achieved by a one-pot reaction with two equivalents of 1,6-dibromohex-3-yne (**8**)^[5] and one equivalent of 1,8-diamino-3,6-dioxaoctane (**9**). Both components were heated in acetonitrile with a surplus of ground potassium carbonate to afford **7** in 40% yield (Scheme 1). The rather high yield of this three-component reaction we ascribe to a fixation of **9** by a potassium ion in a conformation where an intramolecular ring closure is favored over an intermolecular one.^[6,7] The yields with lithium carbonate and cesium carbonate turned out to be much less than with potassium carbonate.

The structure of **7** was confirmed by X-ray investigations on single crystals. The results revealed the *in/in* conformation for both nitrogen atoms.^[8,9] The molecule adopts noncrystallographic C_2 symmetry. The two triple bonds are inclined towards each other by 55° . The intramolecular distance of the nitrogen atoms amounts to 5.49 \AA which is longer than in **4** (4.87 \AA). The molecular structure of **7** is shown in Figure 2. The oxygen atoms of the ether bridge



Scheme 1.

point outwards. The longer ether bridge as compared to the 3-hexyne bridge in **1** gives **7** more flexibility. This shows up when **7** is oxidized with hydroperoxide. The resulting *N,N'*-oxide **10** now adopts the *out/out* conformation at the bridgeheads (Scheme 2, Figure 2). The N–O groups are tilted by 46° relative to the N···N axis and the ether oxygen atoms point inside the cavity.

Figure 2. Molecular structures of **7** (top) and **10**.

Scheme 2.

To probe the complexation properties of **7** we reacted this ligand with silver(I) and copper(I) triflates in dichloromethane and with lithium perchlorate, sodium nitrate, and

cadmium nitrate in methanol. In all five experiments we obtained a colorless crystalline powder which allowed us to grow single crystals for X-ray investigations.

In Table 1 we list the most relevant distances and angles of the metal complexes of **7**. In Figure 3 we show a side view of the molecular structures. It is seen that the small copper ion prefers a close contact with the nitrogen centers and the triple bonds. No contact with the oxygen atom can be observed. As a consequence the N···N distance is shortened to 4.12 Å as compared to the 5.49 Å of the free ligand. The distances between the copper ion and the center of the triple bonds amount to 2.34 and 2.55 Å. These values are larger than the copper alkyne distances reported for copper–alkyne complexes^[10,11] (1.87–2.00 Å) but similar to those found in the copper complex of **1** (2.46–2.57 Å).^[1b] We also notice a lowering of the stretching frequencies found for the triple bonds in the Raman spectrum for [7·Cu]⁺ as compared to **7**. A criterion for the preference of the alkyne units over the oxygen centers is the N–Cu–N angle of 170.6°.^[12]

Table 1. Most relevant distances, angles, and wave numbers in the Ag⁺, Cu⁺, Li⁺, Na⁺, and Cd²⁺ cryptates with **7**. The distances are given in Å and the angles in degrees.^[12]

Compound	[7·Cu] ⁺	[7·Ag] ⁺	[7·Li] ⁺	[7·Na] ⁺	[7·Cd] ²⁺	7
N···N	4.116	4.827	4.337	4.930	4.678	5.485
N···M	2.063	2.423	2.211	2.585	2.417	
	2.066	2.468	2.212	2.590	2.408	
O···M	3.227	2.639	2.080	2.389	2.409	
	3.634	2.716	2.095	2.412	2.459	
π···M	2.342	2.640	2.676	2.733	2.775	
	2.545	2.650	2.744	2.977	2.611	
M···ONO ₂ [−]				2.425	2.263	
N···M···N ^[10]	170.6	198.5	202.6	215.4	208.4	
$\tilde{\nu}$ C≡C ^[a]	2268		2285	2284	2282	2293
Raman	2230	2273		2225	2226	2227
	2203	2207				

[a] cm^{−1}.

The larger silver ion prefers a coordination with N, O, and the triple bonds. The flexible ether chain in **7** has now changed its conformation in such a way that the oxygen centers point inside the cavity. The N···N distance is longer than in the copper complex (Table 1) and the N–Ag–N angle amounts to 198.5°.^[12] The distance between the silver ion and the center of the triple bonds amounts to 2.64–2.65 Å. This value is longer than that reported for cyclic alkynes (2.33 Å)^[10,13] and also longer than that reported for [1·Ag]⁺ (2.44–2.51 Å). The N–Ag distances (2.42, 2.47 Å) are somewhat longer with regard to the value found for **1** (2.31 Å) but rather expanded compared to values reported for homoleptic two coordinated silver(I) amine complexes

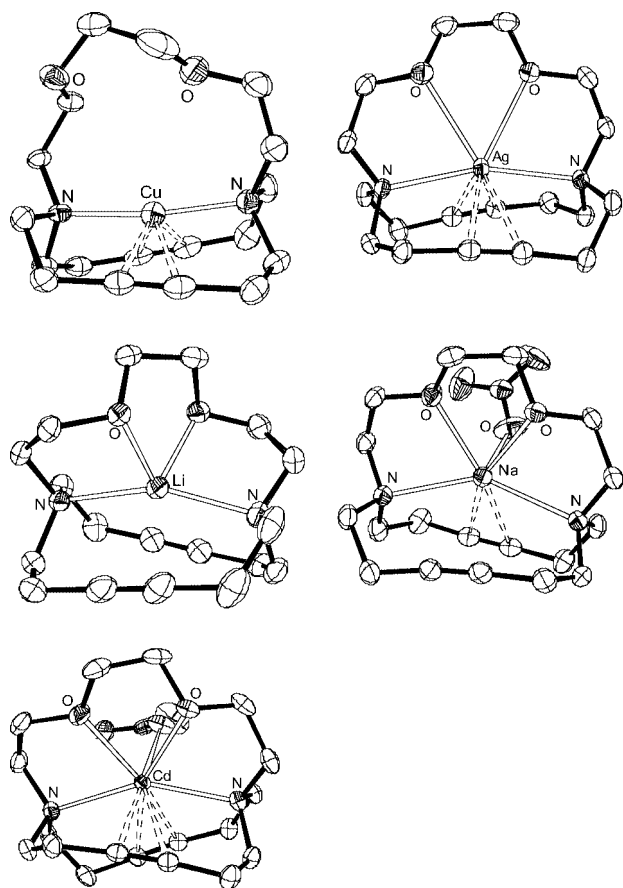


Figure 3. Molecular structures of the Cu^+ , Ag^+ , Li^+ , Na^+ , and Cd^{2+} complexes of **7**. In the cases of the Na^+ and Cd^{2+} complexes the coordinated nitrate anion is shown.

e.g. $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ (2.12 Å).^[14] The silver-alkyne interaction in $[\text{7}\cdot\text{Ag}]^+$ also shows up in a lowering of the wave number of the stretching vibration of the triple bond (Table 1). The $\text{Ag}-\text{O}$ -distance (2.64–2.72 Å) is close to that reported for other silver-ether complexes (average value 2.59 Å).^[15] The complex $[\text{7}\cdot\text{Ag}]^+$ is rather stable. We could not detect any precipitate of silver iodide when we reacted $[\text{7}\cdot\text{Ag}]^+$ with iodide ions. Such an absence of precipitation was also reported for $[\text{1}\cdot\text{Ag}]^+$ and silver salts of aza-bridged macrocycles.^[16]

The lithium ion prefers to coordinate with the nitrogen and oxygen centers. This shows up in the short $\text{Li}-\text{O}$ (2.09 Å) and $\text{Li}-\text{N}$ (2.21 Å) distances and a $\text{N}-\text{Li}-\text{N}$ angle of 202.6°. The measured $\text{Li}-\text{O}$ and $\text{Li}-\text{N}$ distances are close to those reported for lithium crown ether complexes (average value $\text{Li}-\text{O} = 2.02$ Å, $\text{Li}-\text{N} = 2.07$ Å).^[15] We also do not find any significant change for the stretching vibration of the triple bond in $[\text{7}\cdot\text{Li}]^+$. The sodium ion prefers a coordination sphere with six donor groups: The two ether oxygen atoms ($\text{Na}-\text{O} = 2.39, 2.41$ Å), the two nitrogen atoms ($\text{Na}-\text{N} = 2.59$ Å), one oxygen atom from the nitrate anion ($\text{Na}-\text{O} = 2.43$ Å) and one alkyne unit (Na^+ to the center of triple bond = 2.73 Å). This latter interaction hardly has any influence on the stretching vibration of the triple bond. The recorded $\text{Na}-\text{O}$ and $\text{Na}-\text{N}$ distances are

close to those found in sodium crown ether complexes (average value $\text{Na}-\text{O} = 2.47$ Å, $\text{Na}-\text{N} = 2.59$ Å).^[15] The even larger Cd^{2+} ion adopts a coordination number of seven by interacting with all donor units. The $\text{N}-\text{Cd}-\text{N}$ angle of 208.4° shows that the N,O coordination is preferred over the interaction with the triple bonds. The latter at most weakly influences the stretching vibration of the triple bonds (Table 1). The complex $[\text{7}\cdot\text{Cd}]^{2+}$ shows a significant low field shift of the resonances for the CH_2 protons as compared to **7** by 0.2–0.4 ppm. Like in the sodium complex the metal in $[\text{7}\cdot\text{Cd}]^{2+}$ coordinates with one oxygen center of the nitrate anion ($\text{Cd}-\text{O} = 2.23$ Å).

The reaction of a solution of **7** in methanol with HgCl_2 yielded first a colorless precipitate which was insoluble in all common solvents. In analogy to a protocol described by Pickardt and Kühn^[17] we carefully added to an aqueous solution of HgCl_2 a solution of the ligand **7** in methanol in such a way that the two solutions formed two layers. After one month crystals appeared between the two phases. Unfortunately, the crystals were insoluble in common solvents. The mass spectrum revealed that we are dealing with an adduct of **7** with two equivalents of water, three mercury cations, and two chloride anions. The IR spectrum revealed two intensive peaks in the CO region. Fortunately, the isolated material, **11**, contained single crystals which allowed a diffraction experiment. In Figure 4 we show a side view and a view along the $\text{N}\cdots\text{N}$ axis of **11**. The molecule contains one central mercury atom bound to the two nitrogen centers, to two carbon atoms adjacent to the CO groups and to the two oxygen atoms of the ether bridge (Scheme 3). To the former sp centers, adjacent to the CO groups two further HgCl units are attached which point outwards. The distances between the central mercury atom and the ether oxygen atoms amount to 2.87 and 2.97 Å. These values are somewhat longer than that reported for the mean distance between Hg^{2+} and ether (2.83 Å).^[15] The $\text{Hg}-\text{N}$ distances (2.61 and 2.62 Å) are also longer than the mean value reported in the literature (2.35 Å).^[15] Of interest are the short bonds between both Hg centers and the carbon atoms in the α position to the CO groups. For the central mercury we find $\text{Hg}-\text{C}$ distances of 2.22 and 2.17 Å. For the HgCl groups the $\text{C}-\text{Hg}$ distances are even shorter (2.08 and 2.11 Å). We ascribe the longer $\text{C}-\text{Hg}$ bond for the central metal to the donor effects of the oxygen and nitrogen atoms. The low stretching frequencies recorded for the CO groups (1601, 1551 cm^{-1}) point to a delocalization of the formal negative charge at the carbon atoms in the α positions to the CO groups. We find a distance between the central and the peripheral mercury atoms of 3.29 and 3.39 Å. This points to a $d^{10}-d^{10}$ interaction between the metals due to relativistic effects.^[18]

Of special interest is the regioselectivity of the twofold oxymercuration of **7** to **11** which occurred under preservation of the C_2 axis of the molecule. We ascribe this observation to the twisted arrangement of the alkyne units in **7**. To rationalize the regioselectivity we assume that the inclusion of a Hg^{2+} ion into the cavity slows down the interchange between the enantiomeric twist conformations of **7**

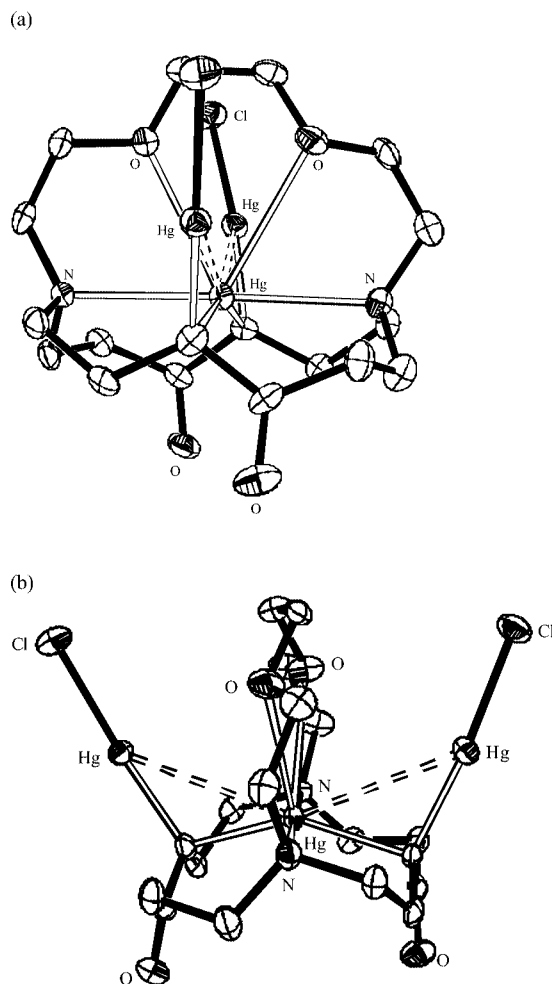
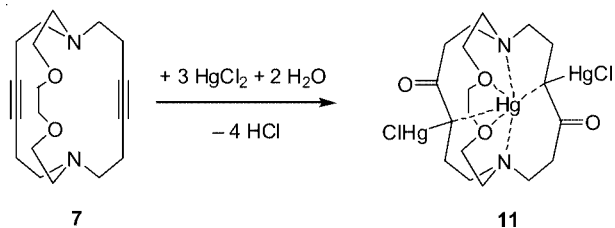


Figure 4. Molecular structure of the product **11** obtained by the reaction of **7** with HgCl_2 in the presence of water.

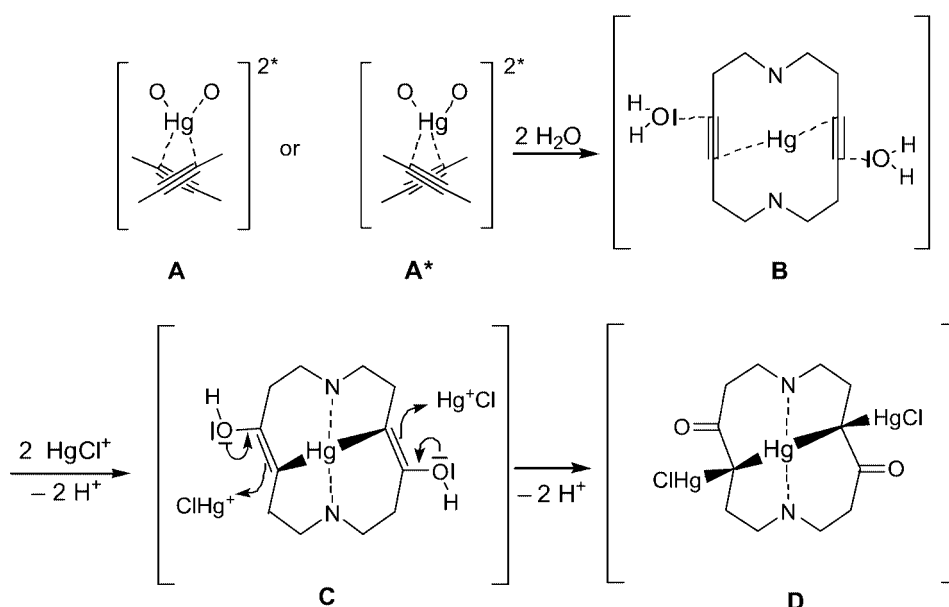


Scheme 3.

(Scheme 4). The coordination of the Hg^{2+} with the ether bridge forces the metal closer to one sp center of one triple bond than to the other (**A**, **A***). Supported by water molecules an *endo*-mercuration starts (**B**) followed by the addition of water (**C**) and *exo*-mercuration of the vinyl alcohol to **D**. In connection with the proposed mechanism in Scheme 4 it is interesting to note that we found single crystals with both enantiomers of the product.

Concluding Remarks

The replacement of one 3-hexyne unit in **1** by the 3,6-dioxaoctane unit gives the resulting cryptand **7** more flexibility and more coordination possibilities. The higher flexibility is also demonstrated by the oxidation of **7** to **10**. A look at the five structures in Figure 2 shows that the hard ions (Li^+ , Na^+ , and to some extent Cd^{2+}) prefer the complexation with the hard centers (O, N). The soft ion Cu^+ prefers the nitrogen centers and the triple bonds. The larger silver ion adopts a coordination number of six. Only in the cases of the Cu^+ and the Ag^+ complexes is the stretching vibration of the triple bonds altered significantly. In the cryptates shown in Figure 3 the ions are less shielded than in the cryptates of **1**, this is shown in the Na^+ and Cd^{2+} salts where the corresponding anion is coordinated.



Scheme 4.

Experimental Section

General Methods: All melting points are uncorrected. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. UV/Vis absorption spectra were recorded with a Hewlett–Packard HP 8452A Diode-Array spectrometer, IR spectra were recorded with a Bruker Vector 22 FT-IR instrument. The NMR spectra were measured with a Bruker WH 300 or Avance 500 spectrometer (^1H NMR at 300 MHz or 500 MHz and ^{13}C NMR at 75 or 125 MHz) using the solvent as an internal standard (δ). FAB mass spectra refer to data from a JEOL JMS-700 instrument. As matrix for the FAB experiments *m*-nitrobenzyl alcohol was used. All reactions were carried out in dried glassware under argon using dried and oxygen-free solvents. Compound **8** was prepared according to literature procedure^[5] and **9** as well as the inorganic salts were commercially available.

X-ray Crystallographic Study: Data were collected with a Bruker Smart CCD diffractometer at 200 K for **7**, **10**, **11**, $[\text{7}\cdot\text{Cu}]^+$, $[\text{7}\cdot\text{Ag}]^+$, $[\text{7}\cdot\text{Na}]^+$ and with a Nonius CAD 4 diffractometer at 293 K for $[\text{7}\cdot\text{Li}]^+$ and 223 K for $[\text{7}\cdot\text{Cd}]^{2+}$. Mo- K_α radiation was used in all cases and the intensities were corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct methods and refined against F^2 with a full-matrix least square algorithm by using the SHELXTL software package.^[19] Relevant crystal and data collection parameters are given in Tables 2 and 3. Hydrogen atoms were refined isotropically for **7** and $[\text{7}\cdot\text{Li}]^+$ and in all other cases they were considered at calculated positions and refined using appropriate riding models. In the case of **10**, **11**, $[\text{7}\cdot\text{Li}]^+$, and $[\text{7}\cdot\text{Cd}]^{2+}$ some solvent molecules or anions had to be treated as disordered, in $[\text{7}\cdot\text{Cu}]^+$ disorder was observed in parts of the complex cation itself. On one side of the cage the three methylene groups next to the nitrogen atom occur in two alternative positions, also the ether bridge is partially affected by disorder. CCDC-277362 (for **7**), -277363 (for **10**), -277364 (for **11**), -277365 {for $[\text{7}\cdot\text{Cu}](\text{CF}_3\text{SO}_3)$ }, -277366 {for $[\text{7}\cdot\text{Ag}](\text{CF}_3\text{SO}_3)$ }, -277367 {for $[\text{7}\cdot\text{Li}](\text{CLO}_4)$ }, -277368 {for $[\text{7}\cdot\text{Na}](\text{NO}_3)$ }, and -277369 {for $[\text{7}\cdot\text{Cd}](\text{NO}_3)_2$ } contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4,7-Dioxa-1,10-diazabicyclo[8.6.6]docosa-13,19-diyne (7): To a suspension of finely ground dry potassium carbonate (16 g) in dry acetonitrile (500 mL) was added 1,6-dibromo-3-hexyne (**8**) (6.3 g, 26.2 mmol) and 1,8-diamino-3,6-dioxaoctane (**9**) (1.3 g, 8.3 mmol) and it was refluxed for 4 d. After cooling of the mixture the residual potassium carbonate was filtered off and the solvent was removed in vacuo. The raw material of the reaction was chromatographed on ALOX III using cyclohexane/ethyl acetate (1:1) as the solvent. The product was recrystallized from ethyl acetate to yield colorless crystals (1.1 g, 43%) with a m.p. of 68 °C. ^1H NMR (500 MHz, CD_3OD): δ = 2.26 (m, 8 H, $\text{CH}_2\text{--C}\equiv$), 2.43–2.52 (m, 12 H, $\text{CH}_2\text{--N}$), 3.63 (m, 4 H, $\text{CH}_2\text{--O}$), 3.78 (s, 4 H, $\text{O--CH}_2\text{--CH}_2\text{--O}$) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 20.0 ($\text{CH}_2\text{--C}\equiv$), 55.7 (4, $\text{CH}_2\text{--N}$), 58.0 (2, $\text{CH}_2\text{--N}$), 71.5 ($\text{CH}_2\text{--O}$), 72.1 ($\text{O--CH}_2\text{--CH}_2\text{--O}$), 80.5 ($\text{C}\equiv\text{C}$) ppm. IR (KBr): $\tilde{\nu}$ = 2937, 2903, 2803, 2740, 1459, 1334, 1291 cm^{-1} . Raman (neat): $\tilde{\nu}$ = 2957, 2903, 2821, 2292, 2227, 1457, 1419 cm^{-1} . $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_2$ (304.43): calcd. C 71.02, H 9.27, N 9.20; found C 71.23, H 9.21, N 9.27.

4,7-Dioxa-1,10-diazabicyclo[8.6.6]docosa-13,19-diyne *N,N'*-Dioxide (10): To a solution of **7** (37 mg, 0.1 mmol) in ethanol (5 mL) was added hydrogen peroxide (1 mL, 30%) solution in water at room temperature. After stirring for 6 d a colorless precipitate was found.

After separation and recrystallization from methanol/water colorless crystals were obtained (23 mg, 60%), m.p. 145 °C (decomp.). ^1H NMR (300 MHz, CD_3OD): δ = 2.79 (m, 8 H, $\text{CH}_2\text{--C}\equiv$), 3.61–3.93 (m, 16 H, CH_2), 3.65 (s, 4 H, $\text{O--CH}_2\text{--CH}_2\text{--O}$) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 15.8 ($\text{CH}_2\text{--C}\equiv$), 65.9 ($\text{N--CH}_2\text{--CH}_2\text{--C}\equiv$), 66.1 ($\text{N--CH}_2\text{--CH}_2\text{--O}$), 71.5 ($\text{CH}_2\text{--O}$), 81.2 ($\text{C}\equiv\text{C}$) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 1435, 1351, 1246 cm^{-1} . HRMS (FAB⁺) $\text{C}_{18}\text{H}_{29}\text{N}_2\text{O}_4$ calcd. 337.2127; found 337.2132.

4,7-Dioxa-1,10-diazabicyclo[8.6.6]docosa-13,19-diyne (7) Complex with Silver Triflate: In a Schlenk tube a solution of **7** (50 mg, 0.16 mmol) and silver(I) triflate (43 mg, 0.17 mmol) in dry dichloromethane (6 mL) was stirred for 3 h at room temperature under argon. The silver triflate complex (90 mg, 100%) of **7** was isolated in quantitative yield as a colorless powder, m.p. 165 °C (decomp.). ^1H NMR (300 MHz, CDCl_3): δ = 2.46–2.59 (m, 16 H, $\text{N--CH}_2\text{--CH}_2\text{--C}\equiv$), 2.69 (t, 3J = 4.8 Hz, 4 H, $\text{CH}_2\text{--N}$), 3.56 (t, 3J = 4.8 Hz, 4 H, $\text{N--CH}_2\text{--CH}_2\text{--O}$), 3.66 (s, 4 H, $\text{O--CH}_2\text{--CH}_2\text{--O}$) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 17.9 ($\text{CH}_2\text{--C}\equiv$), 53.7 ($\text{N--CH}_2\text{--CH}_2\text{--C}\equiv$), 55.2 ($\text{CH}_2\text{--N}$), 66.5 ($\text{N--CH}_2\text{--CH}_2\text{--O}$), 69.8 ($\text{O--CH}_2\text{--CH}_2\text{--O}$), 78.2 ($\text{C}\equiv\text{C}$) ppm. IR (KBr): $\tilde{\nu}$ = 2963, 2904, 1453, 1363 cm^{-1} . Raman (neat): $\tilde{\nu}$ = 2910, 2859, 2273, 2207, 1452, 1335 cm^{-1} . HRMS (FAB⁺) $\text{C}_{18}\text{H}_{28}^{109}\text{AgN}_2\text{O}_2$: calcd. 413.1198, found: 413.1221. $\text{C}_{18}\text{H}_{28}^{107}\text{AgN}_2\text{O}_2$: calcd. 411.1201, found: 411.1212. $\text{C}_{19}\text{H}_{28}\text{AgF}_3\text{N}_2\text{O}_5\text{S}$ (561.37): calcd. C 40.65, H 5.03; found C 40.65, H 5.33.

4,7-Dioxa-1,10-diazabicyclo[8.6.6]docosa-13,19-diyne (7) Complex with Cu^I Triflate: A solution of **7** (30 mg, 0.1 mmol) and the benzene complex of Cu^I triflate (27 mg, 0.1 mmol) in dry dichloromethane (10 mL) was stirred under argon for 3 h at room temperature. Filtration of the precipitate yielded a colorless powder (43 mg, 85%), m.p. 127 °C (decomp.). ^1H NMR (500 MHz, CD_2Cl_2): δ = 2.66 (t, 3J = 5.4 Hz, 8 H, $\text{CH}_2\text{--C}\equiv$), 2.73–2.84 (m, 12 H, $\text{CH}_2\text{--N}$), 3.71 (s, 4 H, $\text{O--CH}_2\text{--CH}_2\text{--O}$), 3.83 (t, 3J = 5.0 Hz, 4 H, $\text{CH}_2\text{--O}$) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 18.3 ($\text{CH}_2\text{--C}\equiv$), 55.6 ($\text{N--CH}_2\text{--CH}_2\text{--C}\equiv$), 55.7 ($\text{CH}_2\text{--N}$), 68.2 ($\text{CH}_2\text{--O}$), 69.7 ($\text{O--CH}_2\text{--CH}_2\text{--O}$), 80.7 ($\text{C}\equiv\text{C}$) ppm. IR (KBr): $\tilde{\nu}$ = 3108, 2962, 2870, 1453 cm^{-1} . Raman (neat): $\tilde{\nu}$ = 2922, 2874, 2268, 2229, 2202, 1454 cm^{-1} . HRMS (FAB⁺) $\text{C}_{18}\text{H}_{28}^{65}\text{CuN}_2\text{O}_2$: calcd. 369.1429; found 369.1419. $\text{C}_{18}\text{H}_{28}^{63}\text{CuN}_2\text{O}_2$: calcd. 367.1446; found 367.1430.

4,7-Dioxa-1,10-diazabicyclo[8.6.6]docosa-13,19-diyne (7) Complex with Lithium Perchlorate: A solution of **7** (50 mg, 0.16 mmol) and lithium perchlorate (15 mg) in dry methanol (5 mL) was stirred for 3 h at room temperature. After removal of the solvent the residue was washed with toluene to yield $7\cdot\text{LiClO}_4$ (42 mg, 63%) as colorless crystals, m.p. 160 °C (decomp.). ^1H NMR (300 MHz, CD_3OD): δ = 2.33 (m, 8 H, $\text{CH}_2\text{--C}\equiv$), 2.51 (m, 8 H, $\text{N--CH}_2\text{--CH}_2\text{--C}\equiv$), 2.56 (t, 3J = 5.2 Hz, 4 H, $\text{N--CH}_2\text{--CH}_2\text{--O}$), 3.66 (t, 3J = 5.2 Hz, 4 H, $\text{N--CH}_2\text{--CH}_2\text{--O}$), 3.78 (s, 4 H, $\text{O--CH}_2\text{--CH}_2\text{--O}$) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 19.8 ($\text{CH}_2\text{--C}\equiv$), 55.5 ($\text{N--CH}_2\text{--CH}_2\text{--C}\equiv$), 57.4 ($\text{N--CH}_2\text{--CH}_2\text{--O}$), 70.6 ($\text{N--CH}_2\text{--CH}_2\text{--O}$), 71.2 ($\text{O--CH}_2\text{--CH}_2\text{--O}$), 80.7 ($\text{C}\equiv\text{C}$) ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2848, 2020, 1464, 1350 cm^{-1} . Raman (neat): $\tilde{\nu}$ = 2931, 2861, 2285, 2228, 1445, 1342 cm^{-1} . HRMS (FAB⁺) $\text{C}_{18}\text{H}_{26}\text{LiN}_2\text{O}_2$: calcd. 311.2311; found 311.2305. $\text{C}_{18}\text{H}_{28}\text{LiN}_2\text{O}_6$ (410.82): calcd. C 52.61, H 6.87, N 6.82; found C 52.44, H 7.19, N 6.70.

4,7-Dioxa-1,10-diazabicyclo[8.6.6]docosa-13,19-diyne (7) Complex with Sodium Nitrate: A solution of **7** (50 mg, 0.16 mmol) and NaNO_3 (14 mg, 0.17 mmol) in dry methanol (5 mL) was stirred at room temperature for 12 h. After removal of the solvent in vacuo the residue was washed with toluene to yield $7\cdot\text{NaNO}_3$ (42 mg, 66%) as colorless crystals, m.p. 165 °C (decomp.). ^1H NMR

Table 2. Crystallographic data and details of the refinement procedure of **7**, **10**, and **11**.

	7	10	11
Empirical formula	C ₁₈ H ₂₈ N ₂ O ₂	C ₁₈ H ₃₈ N ₂ O ₉	C ₁₈ H ₂₈ Cl ₂ Hg ₃ N ₂ O ₅ ·solvent
Formula mass [g/mol]	304.42	426.50	1034.12
Crystal size [mm]	0.44 × 0.32 × 0.22	0.53 × 0.19 × 0.03	0.40 × 0.21 × 0.05
Crystal shape	irregular	polyhedron	polyhedron
Crystal system	triclinic	triclinic	orthorhombic
Space groups	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ 2 ₁ 2
<i>a</i> [Å]	7.5002(4)	8.7957(7)	14.7875(3)
<i>b</i> [Å]	7.9180(4)	10.6449(9)	17.1697(4)
<i>c</i> [Å]	15.0480(7)	13.343(1)	9.5715(2)
α [°]	83.627(1)	109.444(1)	90.00
β [°]	82.697(1)	108.163(1)	90.00
γ [°]	79.153(1)	94.862(1)	90.00
<i>V</i> [Å ³]	867.08(8)	1094.3(2)	2430.17(9)
<i>D</i> _{calcd.} [g/cm ³]	1.166	1.294	2.826
<i>Z</i>	2	2	4
μ [mm ⁻¹]	0.076	0.103	19.157
$\theta_{\min}/\theta_{\max}$	1.37/25.49	1.74/25.55	1.82/27.49
<i>T</i> _{min} / <i>T</i> _{max}	0.77/0.97	0.83/1.00	0.17/0.46
Reflections collected	6530	8210	25114
Reflections unique	2910	3657	5586
Reflections observed	2504	2605	5376
Parameter	311	302	282
<i>R</i> (<i>F</i>)	0.034	0.054	0.030
<i>R</i> _w (<i>F</i> ²)	0.084	0.134	0.076
<i>S</i> (GOF) on <i>F</i> ²	1.05	1.04	1.10
$\Delta\rho_{\max}$ [e·Å ⁻³]/ $\Delta\rho_{\min}$ [e·Å ⁻³]	0.15/−0.18	1.24/−0.20	1.69/−1.89

Table 3. Crystallographic data and details of the refinement procedure of the complexes of **7** with Cu(CF₃SO₃), Ag(CF₃SO₃), LiClO₄, NaNO₃, and Cd(NO₃)₂.

	7 ·Cu(CF ₃ SO ₃)	7 ·Ag(CF ₃ SO ₃)	7 ·LiClO ₄	7 ·NaNO ₃	7 ·Cd(NO ₃) ₂
Empirical formula	C ₁₉ H ₂₈ CuF ₃ N ₂ O ₅ S	C ₁₉ H ₂₈ AgF ₃ N ₂ O ₅ S	C ₁₈ H ₂₈ LiN ₂ O ₂ ·ClO ₄	C ₁₈ H ₃₀ NaN ₃ O ₆	C ₁₈ H ₂₈ CdN ₄ O ₉
Formula mass [g/mol]	517.03	561.36	410.81	407.44	556.8
Crystal size [mm]	0.27 × 0.12 × 0.08	0.40 × 0.14 × 0.06	0.40 × 0.30 × 0.30	0.47 × 0.30 × 0.13	0.40 × 0.30 × 0.01
Crystal shape	polyhedron	polyhedron	needle	polyhedron	polyhedron
Crystal system	triclinic	triclinic	monoclinic	orthorhombic	monoclinic
Space groups	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	8.3241(2)	8.1915(2)	10.296(2)	12.7864(3)	7.710(3)
<i>b</i> [Å]	10.3173(2)	11.3557(4)	15.813(4)	16.2833(2)	20.505(5)
<i>c</i> [Å]	12.9635(1)	12.6963(4)	13.143(4)	19.4195(4)	14.290(4)
α [°]	84.318(1)	107.740(1)	108.67(2)	90.00	90.00
β [°]	85.480(1)	99.277(1)	85.480(1)	90.00	101.88(3)
γ [°]	84.264(1)	91.324(1)	90.00	90.00	90.00
<i>V</i> [Å ³]	1099.64(3)	1106.86(6)	2027.2(9)	4043.2(1)	2211(1)
<i>D</i> _{calcd.} [g/cm ³]	1.56	1.68	1.35	1.34	1.67
<i>Z</i>	2	2	4	8	4
μ [mm ⁻¹]	1.147	1.063	0.23	0.118	1.04
$\theta_{\min}/\theta_{\max}$	1.58/25.55	1.71/25.53	2.1/28.0	2.10/25.50	2.5/28.0
<i>T</i> _{min} / <i>T</i> _{max}	0.81/0.93	0.77/0.94	0.93/0.96	0.82/0.92	0.59/0.76
Reflections collected	8325	8352	5144	28230	5698
Reflections unique	3698	3708	4886	3585	5319
Reflections observed	2814	3434	2883	2693	4226
Parameter	327	280	398	261	337
GOF (<i>F</i> ²)	1.02	1.05	1.03	1.03	1.02
<i>R</i> (<i>F</i>)	0.040	0.021	0.049	0.033	0.037
<i>R</i> _w (<i>F</i> ²)	0.096	0.052	0.133	0.083	0.083
$\Delta\rho_{\max}$ [e·Å ⁻³]/ $\Delta\rho_{\min}$ [e·Å ⁻³]	0.45/−0.41	0.53/−0.44	0.41/−0.32	0.33/−0.20	0.51/−0.63

(500 MHz, CD₃OD): δ = 2.51 (m, 16 H, N-CH₂-CH₂-C≡), 2.70 (t, ³*J* = 5.1 Hz, 4 H, N-CH₂), 3.67 (t, ³*J* = 5.1 Hz, 4 H, CH₂-O), 3.70 (s, 4 H, O-CH₂-CH₂-O) ppm. ¹³C NMR (125 MHz, CD₃OD): δ = 18.8 (CH₂-C≡), 54.0 (N-CH₂-CH₂-C≡), 57.4 (N-CH₂-CH₂-O), 67.7 (N-CH₂-CH₂-O), 70.0 (O-CH₂-CH₂-O), 80.7

(C≡C) ppm. IR (KBr): $\tilde{\nu}$ = 2963, 2914, 2877, 2835, 1456 cm⁻¹. Raman (neat): $\tilde{\nu}$ = 2965, 2918, 2883, 2838, 2284, 2225, 1456 cm⁻¹. HRMS (FAB⁺) C₁₈H₂₈NaN₂O₂: calcd. 327.2048; found 327.2051. C₁₈H₂₈NaN₃O₅ (389.43): calcd. C 55.52, H 7.25, N 10.79; found C 55.23, H 7.42, N 10.42.

4,7-Dioxa-1,10-diazabicyclo[8.6.6]docosa-13,19-diyne (7) Complex with Cadmium Nitrate: A solution of **7** (15 mg, 0.05 mmol) and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (15 mg, 0.05 mmol) in methanol (6 mL) was stirred for 24 h at room temperature. After removal of the solvent a colorless crystalline material (27 mg, 100%) could be isolated which could be recrystallized from methanol and dichloromethane, m.p. 130 °C (decomp.). ^1H NMR (500 MHz, CD_3OD): δ = 2.83 (m, 16 H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{C}\equiv$), 3.12 (s, 4 H, $\text{N}-\text{CH}_2$), 3.89 (m, 4 H, CH_2-O), 3.92 (s, 4 H, $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 18.8 ($\text{CH}_2-\text{C}\equiv$), 53.5 ($\text{N}-\text{CH}_2-\text{CH}_2-\text{C}\equiv$), 58.4 ($\text{N}-\text{CH}_2-\text{CH}_2-\text{O}$), 66.6 ($\text{N}-\text{CH}_2-\text{CH}_2-\text{O}$), 69.5 ($\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$), 84.0 ($\text{C}\equiv\text{C}$) ppm. IR (KBr): $\tilde{\nu}$ = 2931, 2887, 2362, 1664 cm^{-1} . Raman (neat): $\tilde{\nu}$ = 2925, 2827, 2282, 2226, 1457 cm^{-1} . HRMS (FAB^+) $\text{C}_{18}\text{H}_{28}^{114}\text{CdN}_3\text{O}_5$: calcd. 480.1063; found 480.1080. $\text{C}_{18}\text{H}_{28}^{113}\text{CdN}_3\text{O}_5$: calcd. 479.1073; found 479.1095. $\text{C}_{18}\text{H}_{28}^{112}\text{CdN}_3\text{O}_5$: calcd. 478.1056; found 478.1082. Elemental analysis of the dichloride $\text{C}_{18}\text{H}_{28}\text{CdCl}_2\text{N}_2\text{O}_2$ (487.74): calcd. C 44.33, H 5.79, N 5.74; found C 44.19, H 6.01, N 5.83.

Reaction of 4,7-Dioxa-1,10-diazabicyclo[8.6.6]docosa-13,19-diyne (7) with HgCl_2 to Yield 11: To an aqueous solution of HgCl_2 (13 mg, 0.05 mmol) in water (3 mL) was added a solution of **7** (15 mg, 0.05 mmol) in methanol (3 mL) in such a way that the two solutions did not mix. After one month at room temperature we isolated colorless crystals (15 mg, 91%) which were insoluble in all common solvents, m.p. 158 °C. MS (FAB^+): m/z (%) = 1032 (23) $[\text{M} + \text{Na}]^+$, 1010 (84) $[\text{M} + \text{H}]^+$. The calculated isotopic pattern was identical with the obtained one. IR (KBr): $\tilde{\nu}$ = 2832, 1601, 1551, 1455, 1332, 1248, 1179, 1098, 1018 cm^{-1} .

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