

Supplementary material

To compare the conformations of neutral L^1 and L and dications $(L^1H_2)^{2+}$ and $(LH_2)^{2+}$ in complexes, we have generated five pairs that differ by the macrocycle used (L^1 or L). They are: pure ligands, L^1 (**1**) and L ; complexes $L^1(H_2NCS)_2$ (**2**) and $L(H_2NCS)_2$; complexes $(L^1H_2)[ClO_4]_2 \cdot 2H_2O$ (**3**) and $(LH_2)[ClO_4]_2 \cdot 2H_2O$ (**7**); complexes $(L^1H_2)[BF_4]_2$ (**6**) and $(LH_2)[BF_4]_2 \cdot H_2O$; no suitable crystals analogous to **4**(**5**) were obtained upon the interaction of L with Nb_2O_5 (Ta_2O_5) in an aqueous solution of HF , so we have no pair for **4** (**5**).

The available diagrams demonstrate the suitable fit of the atoms forming the macrocyclic cavity and distinctions in the orientation of the pendant arms. The pendant arms reveal the essential mobility in the pure phase of L^1 and L , molecular complexes and in the hydrates. Moreover, the nature of the anion strongly influences the twisting of the pendant group, making it being oriented in opposite directions (complexes **3** and **4**). Only for pair $(L^1H_2)[BF_4]_2$ (**6**) and $(LH_2)[BF_4]_2 \cdot H_2O$, where the intramolecular cation- π interactions are decisive we have found the very close fitting not only for the atoms forming the macrocyclic cavity but also for the pendant arms.

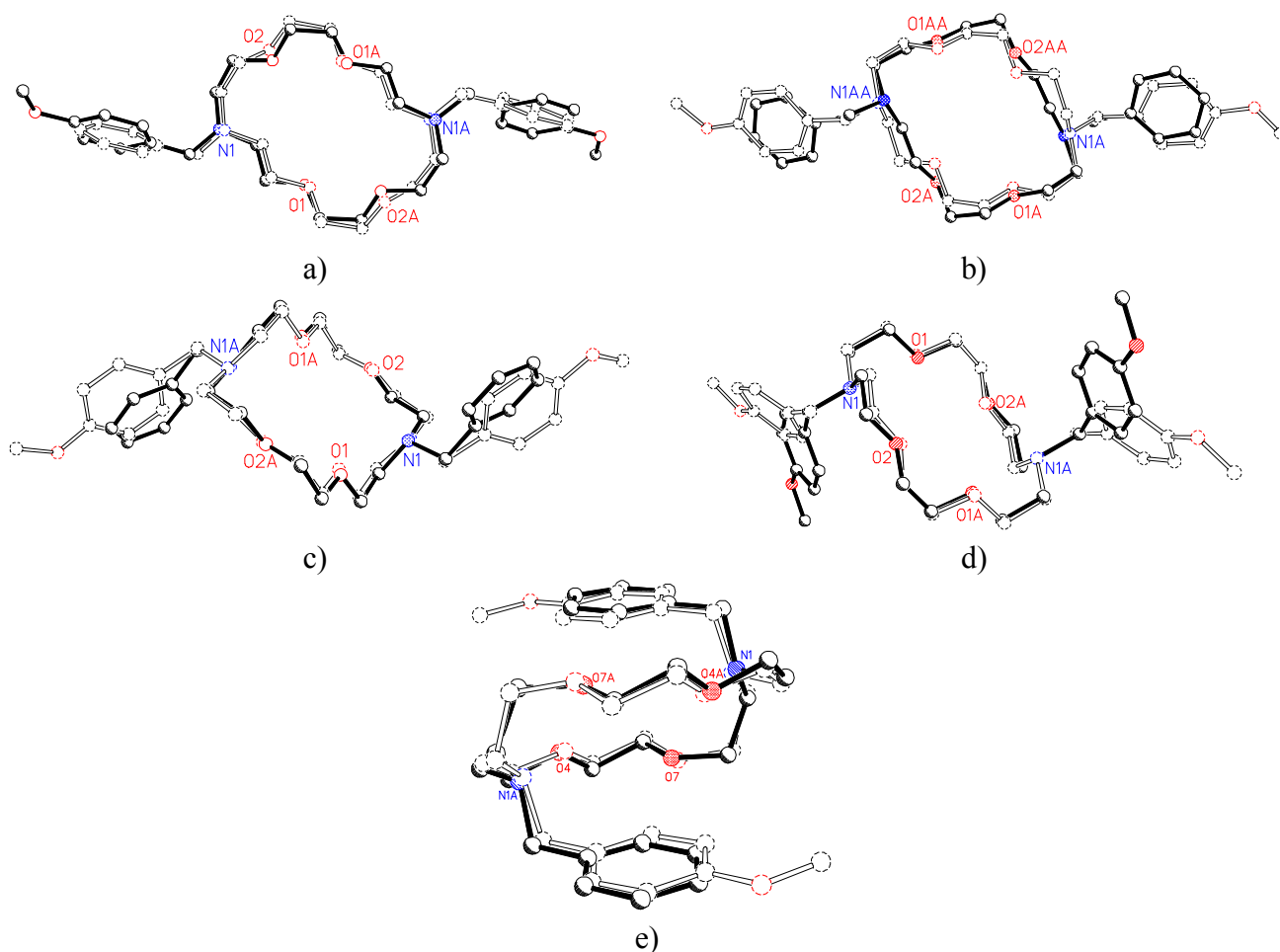


Figure S1. The overlapping diagram for L^1 and L . All H-atoms were omitted for clarity. (a) Free ligands L^1 (present work) and L (cif file with the Refcode XESSUJ01 is taken from CSD) The marked atoms are fitting within ± 0.284 Å. (b) Ligands taken from the complexes $L^1(H_2NCS)_2$ (present work) and $L(H_2NCS)_2$ (of two crystallographically unique macrocycles the conformer more close in conformation to L^1 has been taken).²² The marked atoms are fitting within ± 0.53 Å. (c) $(L^1H_2)^{2+}$ and $(LH_2)^{2+}$ cations taken from $(L^1H_2)[ClO_4]_2 \cdot 2H_2O$ (**3**) and $(LH_2)[ClO_4]_2 \cdot 2H_2O$ (**7**). The marked atoms are fitting within ± 0.132 Å; d) $(L^1H_2)^{2+}$ cations taken from

(L¹H₂)[ClO₄]₂·2H₂O (**3**) and (L¹H₂)[NbF₆]₂·2H₂O (**4**). The marked atoms are fitting with ±0.119 Å; e) (L¹H₂)²⁺ and (LH₂)²⁺ cations taken from (L¹H₂)[BF₄]₂ (**6**) and (LH₂)[BF₄]₂·H₂O. The marked atoms are fitting within ±0.222 Å.

Table 1S. Torsion angles along the macrocyclic framework in L and (LH₂)²⁺ in complexes.

Angle	L	L(H ₂ NCS) 2(A)	L(H ₂ NCS) ₂ (B)	(LH ₂)[ClO ₄] ₂ ·2H 2O (7)	(LH ₂)[BF ₄] ₂ ·H ₂ O.
C(6)-O(1)-C(5)-C(4)	173.2	178.8(6)	-165.5(8)	-177.6(2)	74.0(2)
O(1)-C(5)-C(4)-N(1)	177.1	170.2(6)	-179.9(10)	54.1(3)	60.3(2)
C(5)-C(4)-N(1)-C(1)	-159.2	-174.3(6)	-60.2(10)	-179.5(2)	86.8(2)
C(4)-N(1)-C(1)-C(2)	73.1	51.9(8)	163.0(6)	58.3(3)	-164.0(1)
N(1)-C(1)-C(2)-O(2)	-107.7	57.2(8)	-59.6(9)	63.0(3)	50.1(2)
C(1)-C(2)-O(2)-C(3)	179.1	-178.1(6)	-168.0(7)	-175.6(2)	-165.4(1)
C(2)-O(2)-C(3)-C(6)#1	-139.2	177.3(6)	177.7(7)	-176.2(2)	176.2(1)
O(2)-C(3)-C(6)#1-O(1)#1	69.4	-61.8(9)	-84.6(9)	-64.8(3)	-64.6(2)
C(3)-C(6)#1-O(1)#1-C(5)#1	-171.8	-77.0(8)	77.4(12)	-178.3(2)	-152.6(1)
Symmetry transformation #1	#1 -x,- y+1,-z	#1 -x,- y+1,-z	#3 -x,-y+1,- z+1	#1 -x,-y,-z+1	#1 -x+1,-y,-z+2