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The Role of the C–H···π Interactions in the Cyclisation Reactions Leading to New Aryl-Bridged Tetraazamacrocyclic Complexes of Copper and Nickel

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A series of neutral macrocyclic transition metal complexes of Cu^{II} and Ni^{II}, with bridging polyether linkers joining them to aromatic fragments, has been synthesised and their crystal and molecular structures have been established by single-crystal X-ray diffraction. These molecules adopt an "equatorial" conformation of the bridge due to formation of C–H···π interactions. Because of these interactions only cyclic products are formed in the S_N2 reaction. DFT calculations also confirm experimental results.

Introduction

Molecular recognition occurs due to various intermolecular interactions, such as hydrogen bonding, π···π stacking and electrostatic interactions. An efficient recognition may be achieved by cooperative action of many different interactions. Acceptor···donor interactions of the charge transfer type have recently been utilised in our group to synthesise new catenanes involving +4-charged bismacrocyclic face-to-face complexes containing Ni^{II} and/or Cu^{II} coordinating units. These units interact through a π···π mechanism with electron-rich benzene rings of dibenzo-24-crown-8.[1,2] Changing the oxidation states of the heteronuclear (Ni, Cu) catenane leads to a potential-driven intramolecular motion of the interlocked crown ether molecular fragment.

In all bismacrocycles composed of nearly planar tetraazamacrocyclic components, a face-to-face arrangement of the tetraazamacrocyclic units is observed.[3–8] Sometimes such units are slightly shifted, one relative to the other one. Such molecules form box-like molecular objects that can, and sometimes do, incorporate small guest molecules.

In this work, we incorporate transition metal ions into macrobicyclic receptor molecules composed of a redox switchable, neutral tetraazamacrocyclic complex[9] bridged with a π-electron-rich aromatic linker. We use single-crystal X-ray diffraction measurements to confirm the macrobicyclic structures of the synthesised neutral complexes. In contrast to similar polymethylene bridged macrobicyclic complexes,[10,11] however, the aromatic bridges adopt the "equatorial" conformation due to C–H···π interactions with the saturated part of the molecule and does not form any cavity above the metal-coordinating macrocycle. Apparently, these interactions, although very weak, do influence the conformation of the studied molecules and are an elegant example of the importance of weak C–H···π-electron hydrogen bonds. We also support our experimental findings by theoretical calculations utilising the DFT methods.

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Results and Synthesis

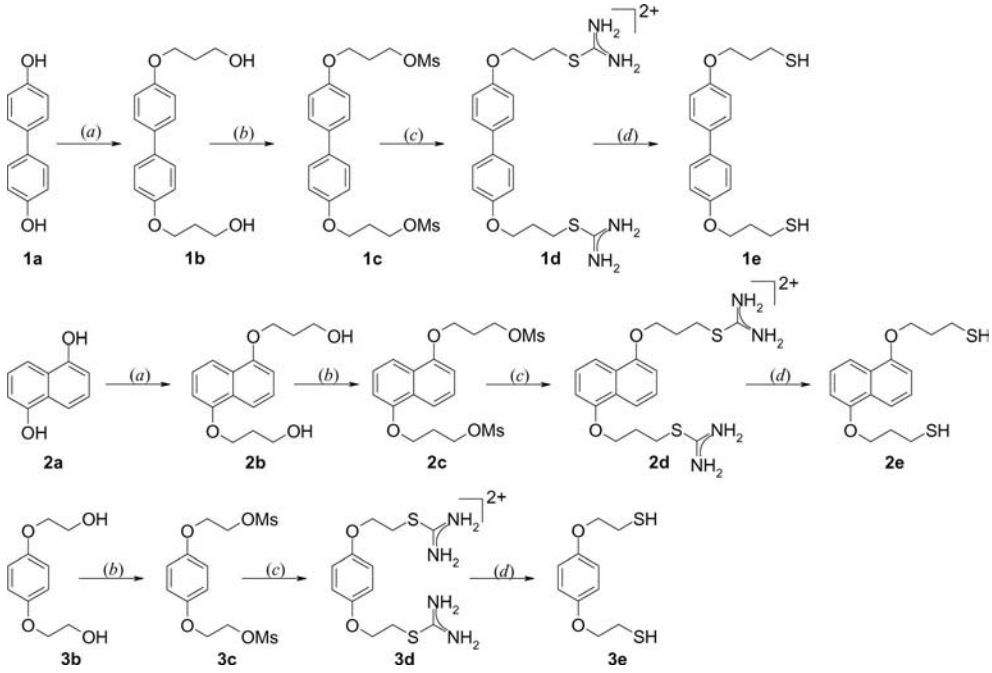
Synthesis

Aromatic dithiols **1e**, **2e** and **3e**, applied as bridging groups, were synthesised from the commercially available compounds **1a**, **2a** and **3b** by using the standard procedures outlined in Scheme 1. Dithiols **1e**, **2e** and **3e**, in the presence of a base, react with symmetric dimesyl (or dichloro) derivatives of neutral macrocyclic complexes of Cu^{II} or Ni^{II} (**4Ni**, **5Ni** and **5Cu**) (Scheme 2) to form the bismacrocyclic-bridged products **CuPh**, **NiPh**, **NiNaph** and **Nibiph**. Even in the presence of an excess of dithiols, only cyclic 1:1 products were isolated from the reaction mixtures and the expected linear 2:1 reaction products were not formed.

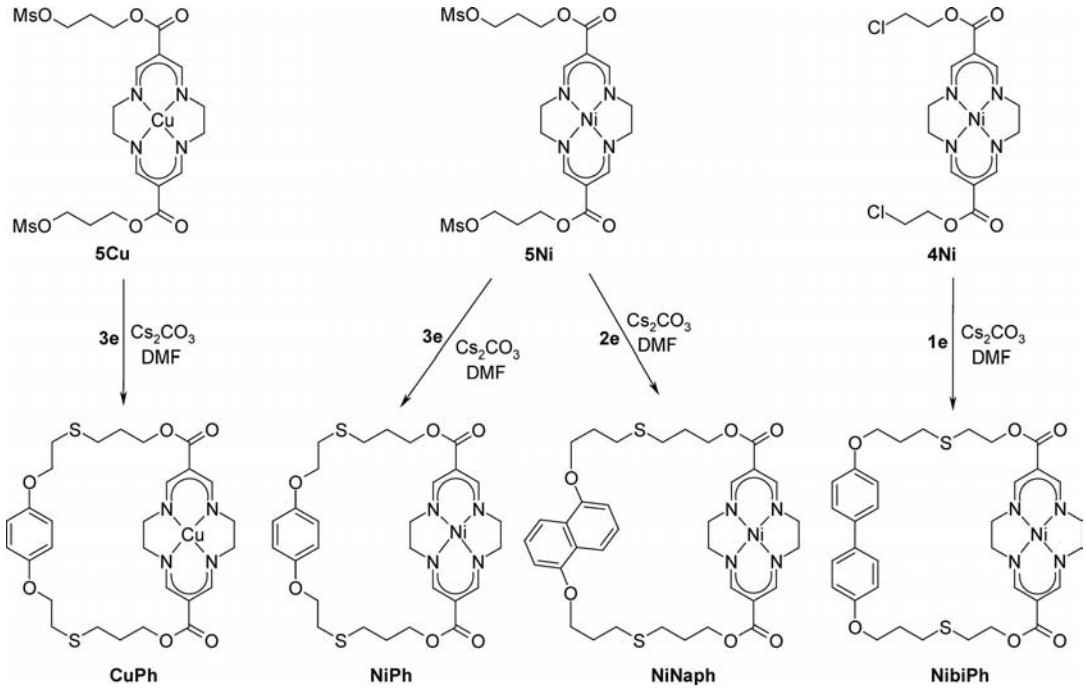
The structures of the isolated bicyclic products were confirmed by elemental analyses, Field desorption mass spectrometry (FDMS), ^1H and ^{13}C NMR spectroscopy (for the diamagnetic Ni^{II} complexes) and single-crystal X-ray crystallography.

X-ray Diffraction Analysis

The atom labelling schemes of bicyclic molecules are shown in Figure 1 and selected geometrical parameters presented in Table 1. The **NiPh** and **NiNaph** compounds crys-



Scheme 1. Synthesis of bridged dithiols. Reagents: (*a*) HO–$(CH_2)_3$–OH; (*b*) MsCl, Et_3N; (*c*) thiourea; (*d*) 1) $NaOH_{(aq.)}$, 2) $HCl_{(aq.)}$ (MsCl = methanesulfonyl chloride).



Scheme 2. Synthesis of aryl-bridged tetraazamacrocyclic complexes of Cu^{II} and Ni^{II}.

tallise in the triclinic $P\bar{1}$ space group with one molecule in the asymmetric unit. **CuPh** and **NibiPh** crystallise in the monoclinic $P2_1/c$ space group with two independent molecules in the asymmetric unit. In all molecules, the angle between respective macrocyclic least-squares planes [Ni(1)N(2)N(3)N(4)N(5)C(6)C(7)C(8)C(11)C(12)C(13) or Ni(01)N(02)N(03)N(04)N(05)C(06)C(07)C(08)C(011)C(012)-C(013)] and the plane containing the aromatic fragment [C(38)C(39)–C(40)C(41)C(42)C(43) or C(038)C(039)-C(040)C(041) C(042)C(043) for **NiPh** and **CuPh**, C(44)-C(45)C(46)C(47)C(48)C(49) or C(044)C(045) C(046)-C(047)C(048)C(049) for **NibiPh**, C(38)C(39)C(40) C(41)-

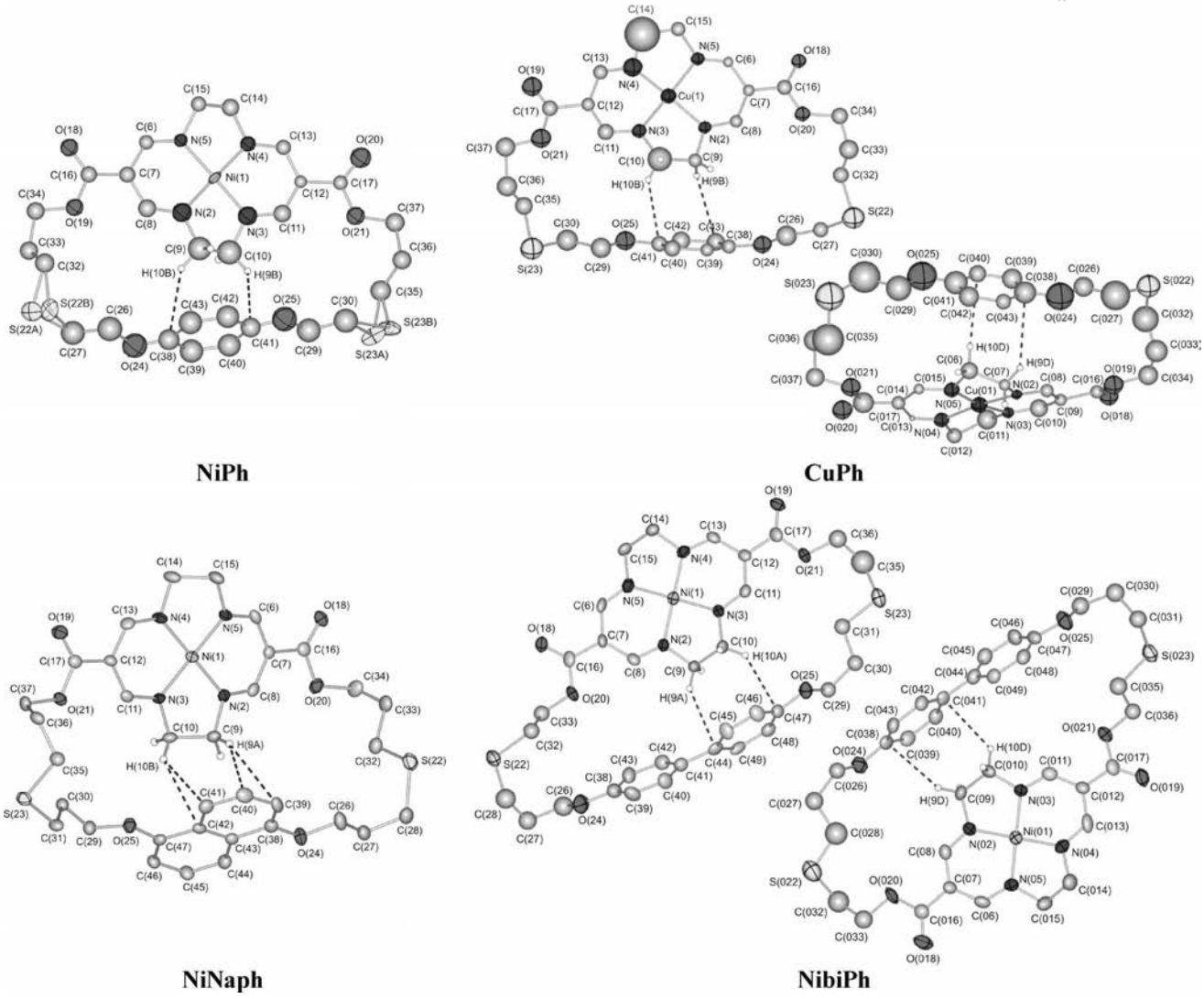


Figure 1. Labelling of atoms and estimation of atomic thermal motion as atomic displacement parameters (ADPs; selected non-hydrogen atoms are treated isotropically; ellipsoids are drawn at 50% probability level). Hydrogen atoms were placed in idealized positions and are omitted for clarity except those involved in C–H···π interactions. Disordered sulfur atoms in the **NiPh** structure are shown as partially transparent. The colours of atoms are the same for all figures.

C(42)C(43) C(44)C(45) C(46)C(46) for **NiNaph**] indicates that these two molecular fragments are nearly perpendicular to each other (the θ_M and θ'_M parameters in Table 1 are close to ca. 70°; the θ'_M is obtained when two symmetry independent molecules are within the asymmetric unit). In the case of **CuPh** and **NiNaph**, the angle is smaller due to the supramolecular arrangement. The metal ion in these complexes forms a square-planar coordination and the M–N bond lengths are typical of this type of compounds (ca. 1.85 Å for **NiPh**, **NibiPh** and **NiNaph**). The Cu–N bond lengths in **CuPh** are slightly longer than the Ni–N ones (ca. 0.06–0.09 Å). The S–C bond lengths are typical, in the range 1.71 Å to 1.93 Å. The benzene rings of the biphenyl moieties in the **NibiPh** structure, described by the angle between two least-squares planes, are twisted by 37.8(3)° and 38.8(3)° for the two symmetrically independent molecules [see parameters θ_P and θ'_P in Table 1 defined as the angles between the planes C(38)C(39)C(40)C(41)C(42)C(43) or C(038)C(039)C(040)C(041)C(042)C(043) and C(44)C(45)-C(46)C(47)C(48)C(49) or C(044)C(045)C(046)C(047)-C(048)C(049), respectively]. The values of these angles are close to the theoretical ones (38.8–45.8°) obtained by means of computational chemistry methods.[12] Additionally, it is worth mentioning that both sulfur atoms in the **NiPh** structure are disordered over two positions with the site occupation ratio 60:40.

The conformation of the molecules seems to be imposed by the C–H···π interactions of the hydrogen atoms from the macrocyclic ethylene bridges to the aromatic rings (Figure 1, Table 2). Apparently, such interactions can work as a template in the cyclisation reactions and they exclude the possibility of the formation of linear products. The proposed mechanism of such a transformation is shown in Scheme 3. The first step is the deprotonation of the SH group and a further S_N2 reaction with the macrocyclic compound. The reaction intermediate formed then undergoes

Table 1. Selected geometrical parameters for the studied compounds.[a].

Parameter θ [°], d [Å]	Compound **NiPh**	**CuPh**	**NibiPh**	**NiNaph**
θ_M	69.9(3)	65.3(5)	76.7(1)	55.73(3)
θ'_M	–	44.5(7)	67.1(2)	–
$d_{M(1)–N(2)}$	1.826(13)	1.910(20)	1.867(5)	1.847(2)
$d_{M(1)–N(3)}$	1.836(13)	1.909(21)	1.858(5)	1.843(2)
$d_{M(1)–N(4)}$	1.816(11)	1.852(25)	1.858(5)	1.846(2)
$d_{M(1)–N(5)}$	1.846(11)	1.949(21)	1.862(5)	1.851(2)
$d_{M(01)–N(02)}$	–	1.978(19)	1.863(5)	–
$d_{M(01)–N(03)}$	–	1.915(20)	1.861(5)	–
$d_{M(01)–N(04)}$	–	1.952(21)	1.854(5)	–
$d_{M(01)–N(05)}$	–	1.919(19)	1.856(5)	–
$d_{S(22)–C(27)}$	1.928(32)	1.737(22)	–	–
$d_{S(22)–C(28)}$	–	–	1.731(8)	1.813(2)
$d_{S(22)–C(32)}$	1.843(25)	1.811(20)	1.857(6)	1.804(2)
$d_{S(23)–C(30)}$	1.709(27)	1.814(25)	–	–
$d_{S(23)–C(31)}$	–	–	1.804(6)	1.801(2)
$d_{S(23)–C(35)}$	1.905(33)	1.809(22)	1.702(9)	1.809(2)
$d_{S(022)–C(027)}$	–	1.729(23)	–	–
$d_{S(022)–C(028)}$	–	–	1.745(8)	–
$d_{S(022)–C(032)}$	–	1.810(21)	1.773(8)	–
$d_{S(023)–C(030)}$	–	1.803(26)	–	–
$d_{S(023)–C(031)}$	–	–	1.811(7)	–
$d_{S(023)–C(035)}$	–	1.816(23)	1.830(7)	–
θ_P	–	–	37.8(3)	–
θ'_P	–	–	38.8(3)	–

[a] M = Ni or Cu; d = distance; in the case of disorder only the major component part is taken into account [for **NiPh** only the S(22A) and S(23A) atoms are considered].

conformational changes from the linear form to the bent one with some extra stabilisation offered by the C–H···π interactions (Scheme 3, a).

Table 2. Geometry of intramolecular C–H···π interactions.[a]

	Interaction	$d_{D–H}$ [Å]	$d_{H···A}$ [Å]	$d_{D···A}$ [Å]	$\theta_{D–H···A}$ [°]
NiPh	C(9)–H(9B)···C(38)$_\pi$	0.99	2.91	3.700(30)	137
	C(10)–H(10B)···C(41)$_\pi$	0.99	2.73	3.520(30)	137
CuPh	C(9)–H(9B)···C(43)$_\pi$	0.99	2.91	3.770(30)	146
	C(10)–H(10B)···C(41)$_\pi$	0.99	2.79	3.630(40)	143
	C(09)–H(09D)···C(038)$_\pi$	0.99	3.04	3.860(30)	141
	C(010)–H(10D)···C(040)$_\pi$	0.99	2.92	3.880(30)	165
NibiPh	C(9)–H(9A)···C(44)$_\pi$	0.99	2.73	3.609(8)	148
	C(10)–H(10A)···C(47)$_\pi$	0.99	2.71	3.388(8)	126
	C(09)–H(9D)···C(038)$_\pi$	0.99	3.06	3.667(8)	121
	C(010)–H(10D)···C(041)$_\pi$	0.99	2.92	3.697(9)	136
NiNaph	C(9)–H(9A)···C(39)$_\pi$	0.99	2.95	3.824(3)	147
	C(9)–H(9A)···C(40)$_\pi$	0.99	2.87	3.769(3)	151
	C(10)–H(10B)···C(41)$_\pi$	0.99	2.79	3.573(3)	137
	C(10)–H(10B)···C(42)$_\pi$	0.99	2.67	3.432(3)	134

[a] D denotes the donor of the D–H···A interaction, A acceptor; C–H···A$_\pi$ stands for the shortest C–H···π contacts.

The next step in the formation of the bismacrocycles is the deprotonation of the remaining SH group, which allows the intramolecular S_N2 reaction to proceed. The same result can be obtained by π···π interactions between the macrocyclic and aryl molecular fragments (Scheme 3, b). However, this possibility is not realised within the crystal structure. A possible justification for this can be found in the supramolecular arrangement. The intramolecular π···π interactions are probably not favourable within the crystalline state due to a large number of other short intermolecular contacts (see Table S1 in the Supporting Information).

The 3D molecular structure of **NiPh** is quite simple and it consists of chains of macrocyclic fragments bound by weak C–H···O interactions. Such chains are weakly connected, which is confirmed by the positions of the disordered sulfur atom and C–H···S contacts. The chain-type moieties form layers (Figure 2), which are held together by weak C–H···π and C–H···O interactions.

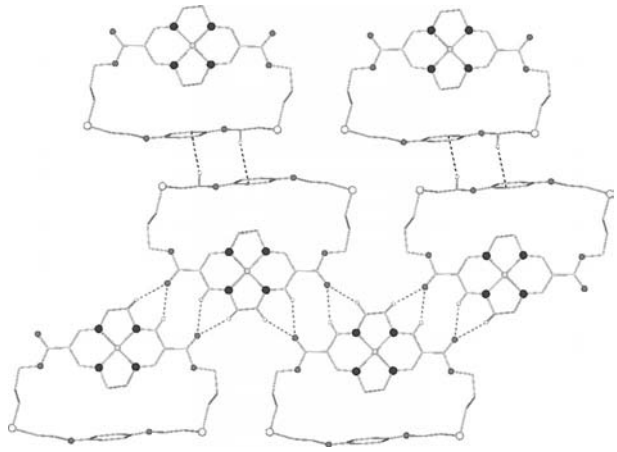
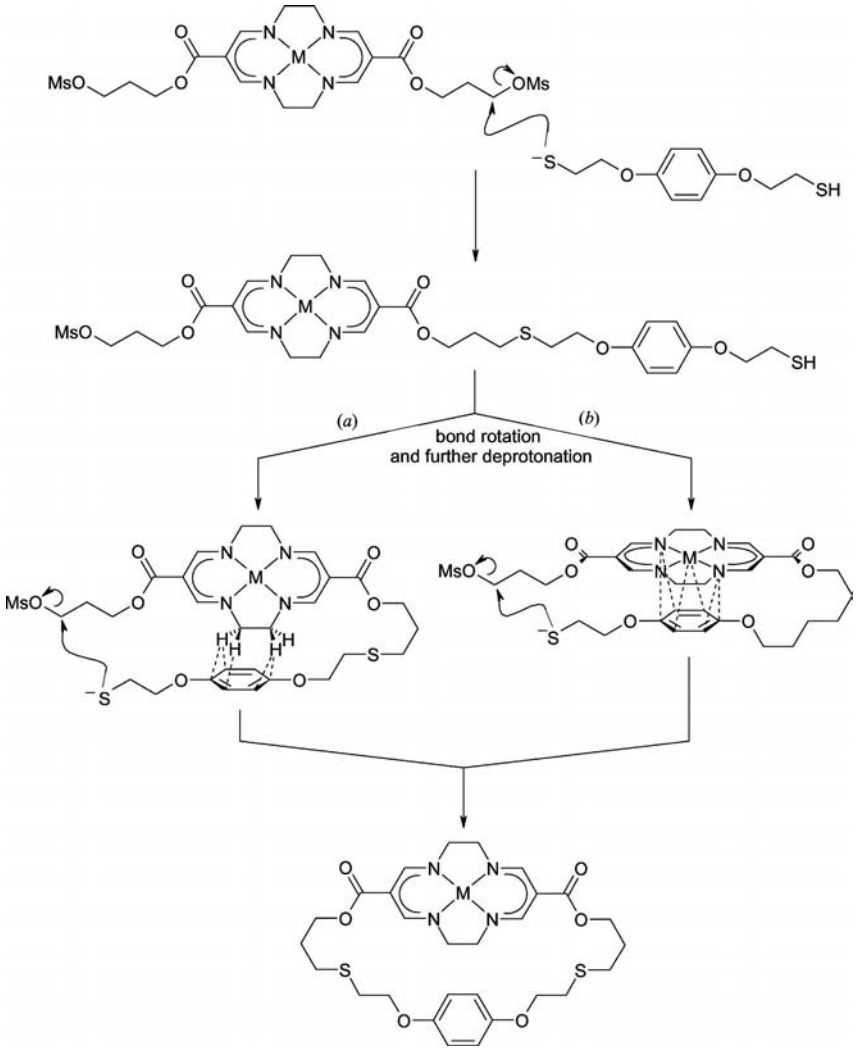


Figure 2. Layers based on C–H···O and C–H···π interactions within the **NiPh** crystal structure.

In the **CuPh** molecular structure, the supramolecular arrangement of molecules is also based on π···π interactions between the macrocyclic fragments of neighbouring symmetry-independent molecules (Figure 3, a). The C–H···π, C–H···O and C–H···S interactions, also present in this structure, serve as a support. In the 3D structure, an interesting intermolecular net is formed with symmetry-independent molecules creating a pseudochain (Figure 3, b). The main difference between the **NiPh** and **CuPh** structures is the number of symmetry independent molecules within the asymmetric unit (one and two, respectively).

The **NibiPh** structure also shows π···π interactions between the macrocyclic fragments. Its supramolecular structure is based on two symmetry independent molecules connected by weak C–H···π interactions between the aromatic and macrocyclic molecular fragments, and C–H···O interactions forming trimeric structures with another molecule (Figure 4, a). Such supramolecular trimers are formed and packed efficiently within the crystal lattice (Figure 4, b). Some weak C–H···S hydrogen bonds are also present and these join together two neighbouring units (Figure 4, c).

In the case of the **NiNaph** structure, C–H···π interactions occur to form dimers (Figure 5, a). The naphthyl rings are bound to the macrocyclic fragments by C–H···π interactions and as a consequence, molecular chains are formed (Figure 5, b). The chains are connected by very weak C–H···O and C–H···S contacts and packed like rods parallel one to another.



Scheme 3. Proposed mechanism of the cyclisation reaction templated by (*a*) C–H···π interactions between the ethylene bridges and aryl group or (*b*) possible π···π interactions between the macrocyclic and aryl molecular fragments (as in **NiPh** or **CuPh**).

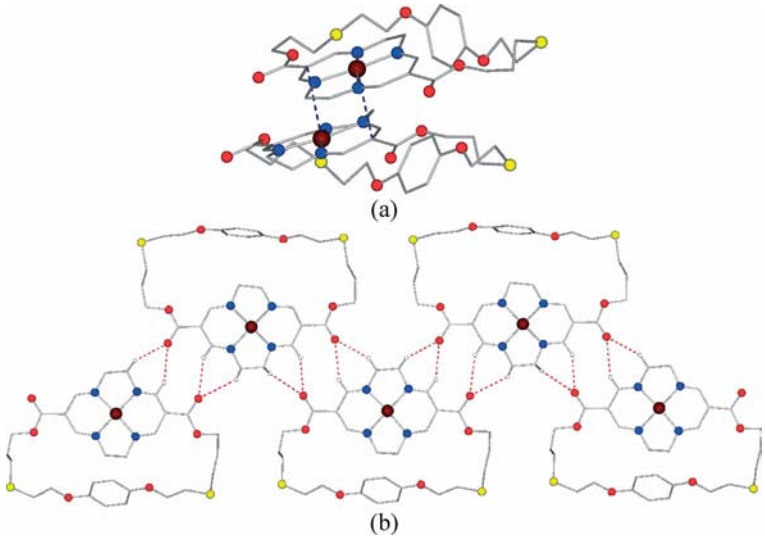


Figure 3. (*a*) The π···π interactions between neighbouring symmetry independent **CuPh** molecules; (*b*) chains of molecules based on weak interactions.

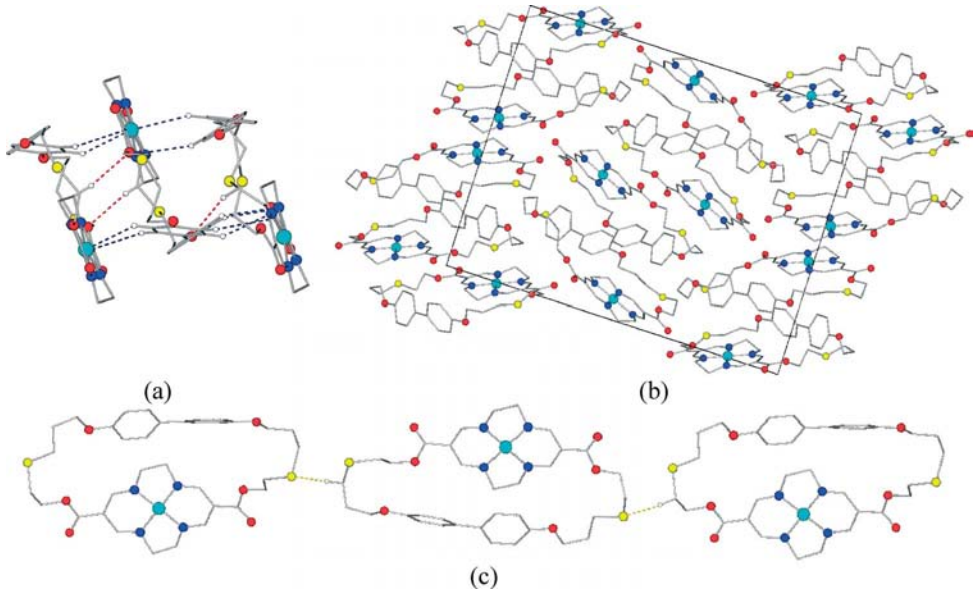


Figure 4. (*a*) Three **NibiPh** molecules connected by C–H···π and C–H···O interactions, (*b*) packing of dimers, (*c*) weak C–H···S interactions between the neighbouring dimers.

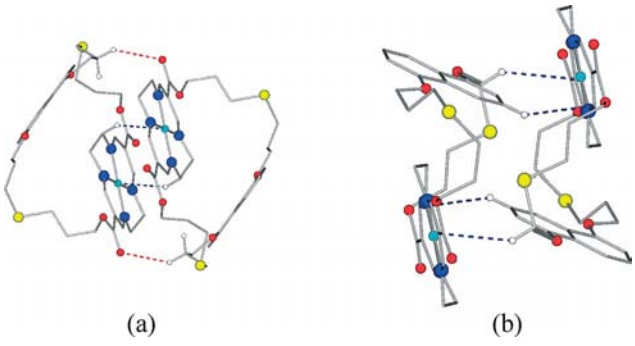


Figure 5. (*a*) Dimers of **NiNaph** in the crystalline state based on C–H···π and C–H···O interactions; (*b*) the structural motif within the chains of molecules based on the C–H···π interactions between the naphthyl rings and the macrocyclic molecular fragment.

Theoretical Calculations

To rationalise the proposed mechanism, quantum-chemical DFT calculations for the **NiPh** compound were carried out with the ADF package.[13] Three possible conformations of the protonated reaction intermediate were taken into account: **K1** – linear, **K2** – bent with assumed C–H···π interactions (starting geometry close to those obtained from crystal structures) and **K3** – bent with assumed π···π interactions between the parallel macrocyclic and phenyl rings with a distance between of approximately 3.5 Å selected as the starting point. The geometries of these three conformers were optimised and their relative energies (ΔE) were calculated and compared (Figure 6). Selected geometrical parameters concerning weak interactions are presented in Table 3.

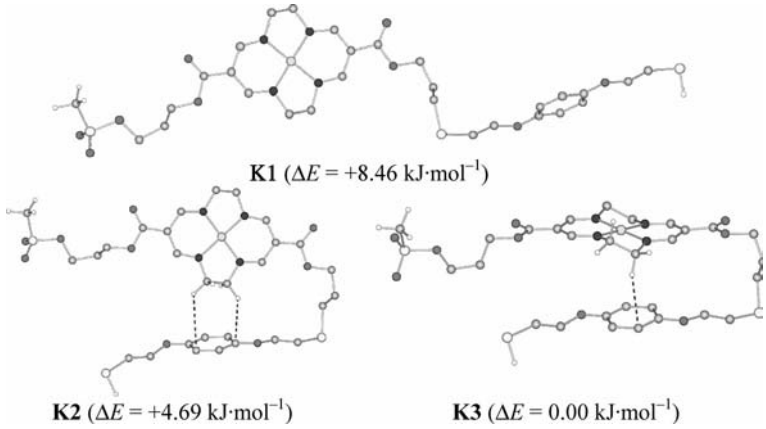


Figure 6. Geometries for three possible conformers (**K1**, **K2** and **K3**) and their relative energies obtained from theoretical calculations. Some hydrogen atoms are omitted for clarity.

Table 3. Selected geometrical parameters for C–H···π interactions for two calculated conformers of **NiPh**.[a]

Conformer	Interaction	$d_{D–H}$ [Å]	$d_{H···A}$ [Å]	$d_{D···A}$ [Å]	$\theta_{D–H···A}$ [°]
K2	C(9)–H(9B)···C(38)$_\pi$	1.100	2.8677	3.6237	125.87
	C(10)–H(10B)···C(41)$_\pi$	1.101	3.4329	4.2461	131.77
K3	C(9)–H(9B)···C(39)$_\pi$	1.103	2.8164	3.8897	164.24

[a] D denotes the donor of the D–H···A interaction, A is the acceptor; D–H···A$_\pi$ denotes the shortest contact of D–H···π interaction.

Although the calculated energy differences between the three conformations are small (probably due to the known restrictions of DFT methods to model weak interactions[14]), several useful features can be found. The two bent conformers **K2** and **K3** are lower in energy than the linear **K1**. After optimisation, the conformer **K3**, the lowest in energy and with π···π interactions (compared to Scheme 2, b), does not show the presence of these interactions and it is stabilised by C–H···π interactions; both bent conformations are stabilised in a similar way. The difference between the bent conformations is caused by different geometry of the weak interaction. In the case of **K3**, the interaction is much closer to linearity than for two cooperative interactions in **K2**. In this case, the presence of π···π interactions is excluded due to a long distance between the macrocyclic and phenyl rings (ca. 4 Å). Therefore, the previously proposed mechanism of the cyclisation reaction should be revised – the π···π interactions in the (b) pathway should be replaced by different geometry of π···π interactions or an additional pathway "(c)" could be introduced (compared to Scheme 2). In fact, all bent conformations led to the products of the cyclisation reaction.

Conclusion

In conclusion, we have prepared a series of neutral macrocyclic transition metal complexes of Cu^{II} and Ni^{II} with bridging polyether linkers joining them to aromatic fragments. We have obtained molecular and crystal structures of four such compounds. It appears that these molecules do not form intramolecular cavities but adopt an "equatorial" conformation of the bridge due to C–H···π interactions. These interactions are responsible for the formation of cyclic products, independent of the ratio of substrates. DFT calculations confirm our experimental findings.

Experimental Section

General: NMR spectra were obtained on Varian Mercury 400 or Varian Gemini 2000BB spectrometers. Signals are reported in ppm relative to the residual solvent signal. IR spectra (paraffin oil mulls) were recorded with a Perkin–Elmer Spectrum 2000 FTIR spectrometer. ESIMS and FDMS were measured on Mariner Perseptive Biosystem and Walters Micromass GCT Premier mass spectrometers, respectively.

Synthesis: Biphenyl-4,4′-diol (**1a**), naphthalene-1,5-diol (**2a**), 1,4-bis(2-hydroxyethoxy)benzene (**3b**), solvents and reagents used in these studies were reagent grade or better. Complexes **5Ni** and **5Cu** were prepared according to procedures described elsewhere.[15]

4,4′-Bis(3-hydroxypropoxy)biphenyl (1b): Biphenyl-4,4′-diol (25 g, 0.134 mol), 3-chloropropan-1-ol (50 mL, 0.598 mol) and Cs_2CO_3 (97.8 g, 0.3 mol) were added to stirred acetonitrile (50 mL). The mixture was refluxed for 6 h and the solids were removed by filtration and washed with warm acetonitrile (3 × 50 mL). The solution was treated with small amount of concentrated $HCl_{(aq.)}$ until it became acidic. The mixture was then partially evaporated and left in the refrigerator for few hours. The crystalline product was then filtered off and washed with cold acetonitrile (3 × 20 mL). The filtrate was again concentrated, crystallised and filtered off. This procedure was repeated few times. The combined solids were dried in vacuo over P_2O_5; yield 23.5 g (58%); m.p. 199–200 °C. IR (nujol): $\tilde{\nu}$ = 3270 (br. s), 1604 (s) cm^{-1}. ^1H NMR ([D$_6$]DMSO, 200 MHz): δ = 1.93 (p, J = 6.0 Hz, 4 H, CH_2 β to OH), 2.65 (t, J = 5.5 Hz, 2 H, OH), 3.67 (q, J = 5.9 Hz, 4 H, CH_2 α to OH), 4.09 (t, J = 6.3 Hz, 4 H, CH_2 γ to OH), 6.96 (m, 4 H, ring CH pos. 2,2′,6 and 6′), 7.50 (m, 4 H, ring CH pos. 3,3′,5 and 5′) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ = 58.1 (CH_2 α to OH), 32.9 (CH_2 β to OH), 65.3 (CH_2 γ to OH), 115.5 (ring CH pos. 3,3′,5 and 5′), 127.9 (ring CH pos. 2,2′,6 and 6′), 132.9 (ring C pos. 1 and 1′), 158.5 (ring CO) ppm.

1,5-Bis(3-hydroxypropoxy)naphthalene (2b): This compound was synthesised from **2a** using the procedure for **1b**; yield 45%; m.p. 139–140 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.27 (q, J = 5.9 Hz, 4 H, CH_2 β to OH), 4.05 (t, J = 6.0 Hz, 4 H, CH_2 α to OH), 4.37 (t, J = 5.9 Hz, 4 H, CH_2 γ to OH), 6.95 (d, J= 7.6 Hz, 2 H, ring CH pos. 4 and 8), 7.44 (t, J = 8.0 Hz, 2 H, ring CH pos. 3 and 7), 7.88 (d, J = 8.7 Hz, 2 H, ring CH pos. 2 and 6) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 32.5 (CH_2 β to OH), 60.8 (CH_2 α to OH), 66.0 (CH_2 γ to OH), 105.8 (ring CH pos. 2 and 6), 114.5 (ring CH pos. 4 and 8), 125.5 (ring CH pos. 3 and 7), 127.0 (ring pos. 9 and 10), 154.2 (ring CO) ppm.

1,4-Bis[2-(methylsulfonyloxy)ethoxy]benzene (3c): 1,4-Bis(2-hydroxyethoxy)benzene (5 g, 25.2 mmol) was suspended in dry dichloromethane (200 mL). Triethylamine (7.7 mL, 55.2 mmol) and methanesulfonyl chloride (4.3 mL, 55.2 mmol) were added with stirring and the resulting mixture was stirred under reflux for 9 h. The solution was washed with water (3 × 75 mL), dried with $MgSO_4$, filtered and partially evaporated to a volume of 50 mL. Hexane (25 mL) was then added and the mixture was heated until dissolution and left in refrigerator. The crude product was recrystallised from a 1:1 mixture of hexane/dichloromethane. The product was filtered off and dried in vacuo; yield 6.37 g (71.3%). IR (nujol): $\tilde{\nu}$ = 1603 (s), 1344 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ = 3.17 (s, 6 H, CH_3), 4.28 (m, 4 H, CH_2-O-), 4.63 (m, 4 H, CH_2OMs), 6.93 (m, 4 H, ring CH) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 38.1 (CH_3), 66.9 (CH_2OMs), 68.4 (CH_2-O-), 116.2 (ring CH), 153.1 (ring CO) ppm.

4,4′-Bis[3-(methylsulfonyloxy)propoxy]biphenyl (1c): The compound was synthesised from **1b** following the procedure used for **3c**; yield 67%; m.p. 132–133 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.25 (q, J = 6.0 Hz, 4 H, CH_2 β to OMs), 3.00 (s, 6 H, S-CH_3), 4.13 (t, J = 5.8 Hz, 4 H, CH_2 γ to OMs), 4.47 (t, J = 6.1 Hz, 4 H, CH_2 α to OMs), 6.95 (m, 4 H, ring CH pos. 2,2′,6 and 6′), 7.47 (m, 4 H, ring CH pos. 3,3′,5 and 5′) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 29.5 (CH_2 β to OMs), 37.6 (S-CH_3), 63.7 (CH_2 α to OMs), 67.1 (CH_2 γ to OMs), 115.1 (ring CH pos. 3,3′,5 and 5′), 128.1 (ring CH pos. 2,2′,6 and 6′), 134.1 (ring C pos. 1 and 1′), 157.9 (ring CO) ppm.

1,5-Bis[3-(methylsulfonyloxy)propoxy]naphthalene (2c): The product was obtained from **2b** according to the procedure for **3c**; yield 78.8%; m.p. 109–110 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.46 (q, J = 6.2 Hz, 4 H, CH_2 β to OMs), 3.04 (s, 6 H, S-CH_3), 4.35 (t, J = 5.8 Hz, 4 H, CH_2 γ to OMs), 4.64 (t, J = 6.1 Hz, 4 H, CH_2 α to OMs), 6.94 (d, J = 7.4 Hz, 2 H, ring CH pos. 4 and 8), 7.45 (t, J = 8.0 Hz, 2 H, ring CH pos. 3 and 7), 7.90 (d, J = 8.5 Hz, 2 H, ring CH pos. 2 and 6) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 29.6 (CH_2 β to OMs), 37.5 (S-CH_3), 63.8 (CH_2 α to OMs), 67.2 (CH_2 γ to OMs), 105.9 (ring CH pos. 2 and 6), 114.7 (ring CH pos. 4 and 8), 125.6 (ring CH pos. 3 and 7), 126.9 (ring C pos. 9 and 10), 154.3 (ring CO) ppm.

***S*,*S*′-*p*-Phenylenebis(1-oxy-2-ethyl)bis(isothiouronium) Di(methanesulfonate) (3d): 3c** (1.62 g, 4.58 mmol) was added to a stirred suspension of thiourea (1.74 g, 22.9 mmol) in ethanol (50 mL). The mixture was refluxed for 4 h and then evaporated to dryness. The solid was suspended in 2-propanol (100 mL) and the mixture was stirred under reflux for 30 min. The product was filtered off, washed well with 2-propanol and dried in vacuo over P_2O_5; yield 2.17 g (93.4%) of colourless crystals; m.p. 100 °C (dec.). ^{1}H NMR (D_2O, 200 MHz): δ = 2.70 (s, 6 H, S-CH_3), 3.44 (br. t, J = 5.2 Hz, 4 H, CH_2-S-), 4.24 (br. t, J = 5.2 Hz, 4 H, CH_2-O-), 6.91 (s, 4 H, ring CH) ppm. ^{13}C NMR (D_2O, 50 MHz): δ = 31.1 (CH_2-S), 38.7 (S-CH_3), 67.9 (CH_2-O-), 116.6 (ring CH), 152.7 (ring CO) ppm.

***S*,*S*′-[4,4′-Biphenylylenebis(1-oxy-3-propyl)]bis(isothiouronium) Di(methanesulfonate) (1d): 1d** was synthesised from **1c** using the same procedure as for **3d**; yield 82%; m.p. 205 °C (dec.). IR (nujol): $\tilde{\nu}$ = 3257 (br. m), 3210 (br. m), 1670 (s) cm^{-1}. ^{1}H NMR (D_2O, 200 MHz): δ = 2.16 (p, J = 6.1 Hz, 4 H, CH_2 β to S), 2.72 (s, 6 H, S-CH_3), 3.27 (t, J = 6.9 Hz, 4 H, CH_2 α to S), 4.16 (t, J = 5.8 Hz, 4 H, CH_2 γ to S), 7.04 (m, 4 H, ring CH pos. 2,2′,6 and 6′), 7.55 (m, 4 H, ring CH pos. 3,3′,5 and 5′) ppm.

***S*,*S*′-[1,5-Naphthylenebis(1-oxy-3-propyl)]bis(isothiouronium) Di(methanesulfonate) (2d):** The product was synthesised from **2c** following the same procedure as for **3d**; yield 79.6%; m.p. 209–210 °C. ^{1}H NMR [CD_3CN/D_2O (3:1), 200 MHz]: δ = 2.46 (p, J = 6.0 Hz, 4 H, CH_2 β to S), 2.82 (s, 6 H, S-CH_3), 3.54 (t, J = 6.8 Hz, 4 H, CH_2 γ to S), 4.42 (t, J = 5.5 Hz, 4 H, CH_2 α to S), 7.14 (d, J= 7.8 Hz, 2 H, ring CH pos. 4 and 8), 7.59 (t, J = 8.2 Hz, 2 H, ring CH pos. 3 and 7), 8.02 (d, J = 8.5 Hz, 2 H, CH pos. 2 and 6) ppm. ^{13}C NMR [CD_3CN/D_2O (3:1), 50 MHz]: δ = 28.2 (CH_2 β to S), 28.2 (CH_2 α to S), 38.9 (S-CH_3), 66.4 (CH_2 γ to S), 106.4 (ring CH pos. 2 and 6), 114.6 (ring CH pos. 4 and 8), 126.0 (ring CH pos. 3 and 7), 126.7 (ring C pos. 9 and 10), 154.3 (ring CO), 171.7 [S-$C(NH_2)_2^+$] ppm.

1,4-Bis(2-sulfanylethoxy)benzene (3e): 3d (0.528 g, 1 mmol) was dissolved in deoxygenated water (5 mL) under argon. Under vigorous stirring, the mixture was treated with NaOH (1.15 g, 28.8 mmol). The temperature was kept below 20 °C. After 1 h, concentrated hydrochloric acid (4 mL) was added keeping the temperature below 40 °C. After few minutes the precipitated solid was filtered off and washed well with deoxygenated water. The wet precipitate was dried in vacuo over P_2O_5; yield 0.201 g (87.4%); m.p. 64–66 °C (dec.). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.75 (t, J = 8.4 Hz, 2 H, SH), 2.94 (dt, J_1 = 6.4, J_2 = 8.4 Hz, 4 H, CH_2-S-), 4.14 (t, J = 6.4 Hz, 4 H, CH_2-O-), 6.92 (s, 4 H, ring CH) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 24.3 (CH_2-S-), 70.6 (CH_2-O-), 116.1 (ring CH), 153.0 (ring CO) ppm.

4,4′-Bis(3-sulfanylpropoxy)biphenyl (1e): The compound was synthesised from **1d** following the procedure for **3e**; yield 81.2%; m.p. 119–121 °C. IR (nujol): $\tilde{\nu}$ = 2550 (w), 1605 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 1.46 (t, J = 8.3 Hz, 2 H, SH), 2.08 (p, J = 6.5 Hz, 4 H, CH_2 β to SH), 2.73 (q, J = 7.4 Hz, 4 H, CH_2 α to SH), 4.10 (t, J = 6.0 Hz, 4 H, CH_2 γ to SH), 6.95 (m, 4 H, ring CH pos. 2,2′,6 and 6′), 7.48 (m, 4 H, ring CH pos. 3,3′,5 and 5′) ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 21.6 (CH_2 α to SH), 33.8 (CH_2 β to SH), 66.2 (CH_2 γ to SH), 115.1 (ring CH pos. 3,3′,5 and 5′), 127.9 (ring CH pos. 2,2′,6 and 6′), 133.6 (ring C pos. 1 and 1′), 158.4 (ring CO) ppm.

1,5-Bis(3-sulfanylpropoxy)naphthalene (2e): The compound was synthesised from **2d** following the procedure for **3e**; yield 93.4%; m.p. 250 °C (dec.). $C_{16}H_{20}O_2S_2$ (308.45): calcd. C 62.30, H 6.54; found C 61.60, H 6.67. IR (nujol): $\tilde{\nu}$ = 1593 (s), 1269 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.52 (t, J = 8.2 Hz, 2 H, SH), 2.30 (p, J = 6.4 Hz, 4 H, CH_2 β to SH), 2.93 (q, J = 7.4 Hz, 4 H, CH_2 α to SH), 4.33 (t, J = 5.8 Hz, 4 H, CH_2 γ to SH), 6.93 (d, J = 7.6 Hz, 2 H, ring CH pos. 4 and 8), 7.44 (t, J = 8.4 Hz, 2 H, ring CH pos. 3 and 7), 7.90 (d, J = 8.7 Hz, 2 H, ring CH pos. 2 and 6) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 21.8 (CH_2 α to SH), 33.8 (CH_2 β to SH), 66.2 (CH_2 γ to SH), 105.8 (ring CH pos. 2 and 6), 114.6 (ring CH pos. 4 and 8), 125.4 (ring CH pos. 3 and 7), 127.0 (ring C pos. 9 and 10), 154.6 (ring CO) ppm.

{6,13-Bis[(2-chloroethoxy)carbonyl]-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato(2$^-$)-κ^4*N*}nickel(II) (4Ni): The product was synthesised following the procedure for the synthesis of **5Ni**[15] using corresponding diol as a substrate. However, the dichloro derivative was isolated instead of the expected dimesylate; yield 86.3%. IR (nujol): $\tilde{\nu}$ = 1672 (s), 1600 (s), 1548 (m), 761 (m) cm^{-1}. MS (ESI, $CHCl_3$): m/z = 425.3 [$C_{16}H_{20}N_4O_4Cl_2Ni$ – Cl^-], 460.2 ($C_{16}H_{20}N_4O_4Cl_2Ni$ – e^-). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.40 (br. s, 8 H, N-CH_2CH_2-N), 3.72 (t, J = 5.7 Hz, 4 H, CH_2Cl), 4.41 (t, J = 5.7 Hz, 4 H, CH_2-O-), 7.83 (s, 4 H, ring CH-N) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 42.5 (CH_2Cl), 58.7 (N-CH_2CH_2-N), 63.0 (CH_2O), 97.7 (endocyclic, 4 °C), 155.0 (endocyclic CHN), 167.2 (C=O) ppm.

[2,20-Dioxo-1^3,1^6,1^{10},1^{13}-tetraaza-3,10,12,19-tetraoxa-7,15-dithia-1(1,8)-cyclotetradecana-11(1,4)-benzenaeicosacyclophano-1^1,1^6,1^8,1^{13}-tetraenato(2$^-$)-κ^4*N*]nickel(II) (NiPh): The reaction was carried out under argon. **5Ni** (0.152 g, 0.25 mmol) and **3e** (0.058 g, 0.25 mmol) were dissolved in DMF (10 mL) at 50 °C. Cs_2CO_3 (0.25 g, 0.767 mmol) was then added and stirring was continued for 5 h at 50 °C. After this time, concentrated hydrochloric acid (1 mL) in water (50 mL) was added. The orange precipitate was then filtered off and washed several times with small amounts of water. The dry solid was dissolved in dichloromethane. The solution was washed with water and the organic layer was dried with Na_2SO_4. The product was purified on silica gel using CH_2Cl_2/MeOH (99:1) as an eluent. Further purification was carried out by crystallisation from CH_2Cl_2/MeOH upon slow evaporation of solvent. The product was dried in vacuo over P_2O_5; yield 0.032 g (20%). $C_{28}H_{36}N_4NiO_6S_2$ (647.43): calcd. C 51.94, H 5.60, N 8.65; found C 51.74, H 5.51, N 8.89. MS (FD, CH_2Cl_2): m/z = 646.1 [$C_{28}H_{36}N_4O_6S_2Ni$ – e^-], 669.3 ($C_{28}H_{36}N_4O_6S_2Ni$ + Na^+). ^{1}H NMR (CD_3Cl, 200 MHz): δ = 2.10 (br. p, J = 6.0 Hz, 4 H, CH_2 β to CO_2), 2.80 (t, J = 7.1 Hz, 4 H, CH_2 β to O-C_{Ar}), 2.98 (t, J = 8.1 Hz, 4 H, CH_2 γ to CO_2), 3.16 (br. s), 3.35 (br. s, 8 H, N-CH_2CH_2-N), 4.07 (t, J = 7.0 Hz, 4 H, CH_2 α to O-C_{Ar}), 4.31 (br. t, J = 4.6 Hz, 4 H, CH_2 α to CO_2), 7.6 (s, 4 H, CHN) ppm.

[2,20-Dioxo-1^3,1^6,1^{10},1^{13}-tetraaza-3,10,12,19-tetraoxa-7,15-dithia-1(1,8)-cyclotetradecana-11(1,4)-benzenaeicosacyclophano-1^1,1^6,1^8,1^{13}-tetraenato(2$^-$)-κ^4*N*]copper(II) (CuPh): This compound was synthesised from **5Cu** and **3e** following the procedure for **NiPh**; yield 27.8%. $C_{28}H_{36}CuN_4O_6S_2$ (652.28): calcd. C 51.56, H 5.56, N

8.59; found C 51.51, H 5.53, N 8.76. MS (FD, CH_2Cl_2): m/z = 651.2 [$C_{28}H_{36}N_4O_6S_2Cu - e^-$], 674.3 ($C_{28}H_{36}N_4O_6S_2Cu + Na^+$).

[2,21-Dioxo-1^3,1^6,1^{10},1^{13}-tetraaza-3,10,13,20-tetraoxa-6,17-dithia-1(1,8)-cyclotetradecana-11(1,4),12(4,1)-dibenzenaeicosacyclophano-1^1,1^6,1^8,1^{13}-tetraenato(2$^-$)-κ^4 *N*]nickel(II) (NibiPh): The compound was synthesised from **4Ni** and **1e** following the procedure for **NiPh**; yield 29%. $C_{34}H_{40}N_4NiO_6S_2$ (723.53): calcd. C 56.44, H 5.57, N 7.74, S 8.86; found C 56.67, H 5.80, N 7.99, S 9.05. MS (FD, CH_2Cl_2): m/z = 722.2 ($C_{34}H_{40}N_4NiO_6S_2 - e^-$). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.08 (br. p, J = 6.2 Hz, 4 H, CH_2 β to O–C_{Ar}), 2.76 (t, J = 6.4 Hz, 4 H, CH_2 β CO_2), 2.85 (t, J = 7.0 Hz, 4 H, CH_2 γ to O-C_{Ar}), 3.03 (br. s, 8 H, N-CH_2CH_2-N), 4.10 (t, J = 5.8 Hz, 4 H, CH_2 α to O-C_{Ar}), 4.32 (t, J = 6.4 Hz, 4 H, CH_2 α to CO_2), 6.95 (m, 4 H, biphenyl ring CH pos. 2,2′,6 and 6′), 7.49 (m, 4 H, biphenyl ring CH pos. 3,3′,5 and 5′), 7.63 (s, 4 H, ring CHN) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 28.8 (CH_2 β to O-$C_{ar.}$), 30.0 (CH_2 γ to O-C_{Ar}), 31.7 (CH_2 β to CO_2), 58.8 (N-CH_2CH_2-N), 63.4 (CH_2 α to CO_2), 66.3 (CH_2 α to O-C_{Ar}), 98.3 (endocyclic, 4 °C), 115.3 (biphenyl ring CH pos. 3,3′,5 and 5′), 127.8 (biphenyl ring CH pos. 2,2′,6 and 6′), 133.4 (biphenyl ring CH pos. 1 and 1′), 155.0 (endocyclic CHN), 158.1 (biphenyl ring CO pos. 4 and 4′), 167.6 (C=O) ppm.

[2,22-Dioxo-1^3,1^6,1^{10},1^{13}-tetraaza-3,11,13,21-tetraoxa-7,17-dithia-1(1,8)-cyclotetradecana-12(1,5)-naphthalenadocosacyclophano-1^1,1^6,1^8,1^{13}-tetraenato(2$^-$)-κ^4*N*]nickel(II) (NiNaph): This compounds was obtained from **5Ni** and **2e** using the procedure for **NiPh**; yield 10.2%. $C_{34}H_{42}N_4NiO_6S_2$ (725.54): calcd. C 56.28, H 5.83, N 7.72; found C 56.21, H 5.78, N 7.83. MS (FD, CH_2Cl_2): m/z = 724.1 [$C_{34}H_{42}N_4O_6S_2Ni - e^-$], 747.2 ($C_{34}H_{42}N_4O_6S_2Ni + Na^+$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.00 (br. p, J = 6.2 Hz, 4 H, CH_2 β to CO_2), 2.23(p, J = 6.8 Hz, 4 H, CH_2 β to O-C_{Ar}), 2.74 (t, J = 7.2 Hz, 4 H, CH_2 γ CO_2), 2.80 (br. s, 8 H, N-CH_2CH_2-N-), 2.85 (t, J = 7.1 Hz, 4 H, CH_2 γ to O-C_{Ar}), 4.23 (t, J = 6.3 Hz, 4 H, CH_2 α to O-C_{Ar}), 4.26 (t, J = 5.3 Hz, 4 H, CH_2 α to CO_2), 6.86 (d, J = 7.6 Hz, 2 H, ring CH pos. 4 and 8), 7.64 (s, 4 H, ring CHN), 7.36 (t, J = 8.0 Hz, 2 H, ring CH pos. 3 and 7), 7.79 (d, J = 8.5 Hz, 2 H, ring CH pos. 2 and 6) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 29.1 (CH_2 β to O-C_{Ar}), 29.5 (CH_2 γ to O-C_{Ar}), 29.5 (CH_2 γ to O-C_{Ar}), 29.6 (CH_2 β to CO_2), 58.3 (N-CH_2CH_2-N), 61.8 (CH_2 α to CO_2), 66.4 (CH_2 α to O-C_{Ar}), 98.0 (endocyclic, 4 °C), 105.3 (ring CH pos. 2 and 6), 114.1 (ring CH pos. 4 and 8), 125.4 (ring CH pos. 3 and 7), 126.5 (naphthalene C pos. 9 and 10), 154.3 (naphthalene ring CO), 154.6 (endocyclic CHN), 167.6 (C=O) ppm.

X-ray: Single crystal X-ray measurements for **NiPh**, **CuPh**, **NibiPh** and **NiNaph** were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) equipped with an Oxford Cryosystems nitrogen gas-flow LT attachment. Crystals were positioned at 62 mm from the KM4CCD camera. The data were corrected for Lorentz and polarisation effects. Data reduction and analysis were carried out with the Oxford Diffraction Ltd. suite of programs. All structures were solved by direct methods using SHELXS-97[16] and refined using SHELXL-97.[16] The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted R factors (wR) and all goodness-of-fit (GooF) values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $F_o^2 > 2\sigma(F_o^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. Scattering factors were taken from International Tables for Crystallography.[17] Most non-hydrogen atoms were refined anisotropically except for some for which their ADPs were not going to real values during the refinement or no reasonable model of disorder could be found (due to the low quality of crystals). All hydrogen atoms were placed in idealised positions. In the case of **CuPh** structure, the AFIX 66 instruction was used during the refinement to restrain the geometry of aromatic rings.

CCDC-770713 (for **CuPh**), -770714 (for **NibiPh**), -770715 (for **NiNaph**), and -770716 (for **NiPh**) 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.

CuPh: $C_{28}H_{36}CuN_4O_6S_2$; molecular weight: 652.27 a.u.; T = 100(2) K; monoclinic; space group, $P2_1/c$; unit cell dimensions, a = 17.345(6) Å, b = 9.2771(17) Å, c = 37.075(9) Å, α = 90°, β = 100.59(2)°, γ = 90°, V = 5864(3) Å^3; Z = 8; d_{calc} = 1.478 g cm^{-3}; absorption coefficient, μ = 0.936 mm^{-1}; $F(000)$ = 2728; crystal size: 0.28 × 0.09 × 0.07 mm^3; θ range for data collection: 2.65–25.00°; index ranges: $-16 < h < 20$, $-11 < k < 11$, $-44 < l < 37$; reflections collected: 22714/unique: 9440 (R_{int} = 0.2644); absorption correction: muti-scan; refinement method: full-matrix least-squares on F^2; goodness-of-fit on F^2, GooF = 0.967; data/restraints/parameters, 9440/16/306; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.1893, $wR2$ = 0.3747; R indices (all data): $R1$ = 0.5007, $wR2$ = 0.4560; weight: $1/[\sigma^2(F_o^2) + (0.0775P)^2 + 0.28P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$; largest diffraction peak and hole: 1.038 and –1.088 e Å^{-3}.

NibiPh: $C_{34}H_{40}N_4NiO_6S_2$; molecular weight: 723.53 a.u.; T = 100(2) K; monoclinic; space group, $P2_1/c$; unit cell dimensions, a = 12.1749(5) Å, b = 20.5721(10) Å, c = 26.5008(11) Å, α = 90°, β = 94.916(4)°, γ = 90°, V = 6613.1(5) Å^3; Z = 8; d_{calc} = 1.453 g cm^{-3}; absorption coefficient, μ = 0.765 mm^{-1}; $F(000)$ = 3040; crystal size: 0.35 × 0.10 × 0.09 mm^3; θ range for data collection: 2.60–28.70°; index ranges: $-16 < h < 16$, $-27 < k < 27$, $-35 < l < 35$; reflections collected: 98058/unique: 16179 (R_{int} = 0.1615); absorption correction: muti-scan; refinement: full-matrix least-squares on F^2; goodness-of-fit on F^2, GooF = 0.832; data/restraints/parameters, 16179/144/748; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0752, $wR2$ = 0.1797; R indices (all data): $R1$ = 0.2056, $wR2$ = 0.2043; weight: $1/[\sigma^2(F_o^2) + (0.0775P)^2 + 0.28P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$; largest diffraction peak and hole: 2.672 and – 1.061 e Å^{-3}.

NiNaph: $C_{34}H_{42}N_4NiO_6S_2$; molecular weight: 725.55 a.u.; T = 100(2) K; triclinic; space group, $P\bar{1}$; unit cell dimensions, a = 11.3728(14) Å, b = 11.8373(12) Å, c = 12.7849(12) Å, α = 88.970(8)°, β = 77.895(9)°, γ = 83.531(9)°, V = 1672.1(3) Å^3; Z = 2; d_{calc} = 1.441 g cm^{-3}; absorption coefficient, μ = 0.756 mm^{-1}; $F(000)$ = 764; crystal size: 0.32 × 0.14 × 0.08 mm^3; θ range for data collection: 2.67– 25.00°; index ranges: $-13 < h < 13$, $-14 < k < 14$, $-15 < l < 15$; reflections collected: 26215/unique: 5886 (R_{int} = 0.0519); absorption correction: muti-scan; refinement method: full-matrix least-squares on F^2; goodness-of-fit on F^2, GooF = 0.786; data/restraints/parameters, 5886/0/424; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0292, $wR2$ = 0.0468; R indices (all data): $R1$ = 0.0622, $wR2$ = 0.0503; weight: $1/[\sigma^2(F_o^2) + (0.0775P)^2 + 0.28P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$; largest diffraction peak and hole: 0.353 and –0.271 e Å^{-3}.

NiPh: $C_{28}H_{36}N_4NiO_6S_2$; molecular weight: 647.44 a.u.; T = 100(2) K; triclinic; space group, $P\bar{1}$; unit cell dimensions, a = 6.6872(18) Å, b = 14.941(4) Å, c = 15.205(3) Å, α = 100.901(19)°, β = 97.514(18)°, γ = 95.49(2)°, V = 1467.6(6) Å^3; Z = 2; d_{calc} = 1.465 g cm^{-3}; absorption coefficient, μ = 0.852 mm^{-1}; $F(000)$ = 680; crystal size: 0.18 × 0.14 × 0.09 mm^3; θ range for data collection: 2.76–25.00°; index ranges: $-7 < h < 7$, $-17 < k < 17$, $-18 < l < 18$; reflections collected: 14598/unique: 5139 (R_{int} = 0.2699); absorption correction: muti-scan; refinement method: full-matrix least-squares on F^2;

goodness-of-fit on F^2, GooF = 0.926; data/restraints/parameters, 5139/27/199; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.1320, $wR2$ = 0.2249; R indices (all data): $R1$ = 0.3367, $wR2$ = 0.3075; weight: $1/[\sigma^2(F_o^2) + (0.0775P)^2 + 0.28P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$; largest diffraction peak and hole: 0.826 and –0.475 e Å^{-3}.

Computational Details: The geometry optimisations, calculations of vibrational frequencies and population analyses were carried out with the ADF2008 package[13] by means of DFT methods with the GGA BP86 functional and ZORA approximation[18] using frozen-core (for optimisation and frequencies) and all-electron (for exact energy calculation) TZP (triple-ζ with polarisation function) basis set as implemented in the package. The vibrational frequencies were computed within the harmonic approximation. The Cartesian coordinates for optimised geometries are presented in the Supporting Information.

Supporting Information (see also the footnote on the first page of this article): Geometrical parameters for selected weak intermolecular interactions in the studied crystal structures, Cartesian coordinates for conformers **K1**, **K2** and **K3** and selected proton and carbon NMR spectra in CD_3Cl solution.

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