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Metallomacrocyclic Complexes by Self-Assembly of Ni^{II} and Cu^{II} Ions and Chelating Bis(*N*-acylamidines)[‡]

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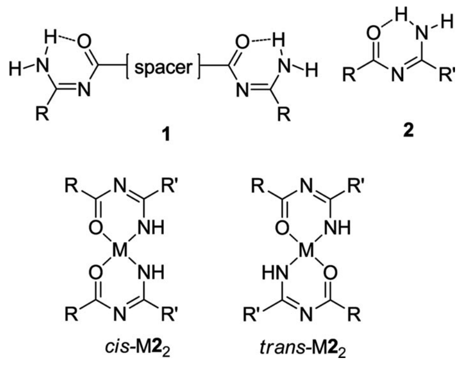
Bis(*N*-acylamidines) **1**, which contain various rigid or flexible spacer units with different spatial orientations, are potent bis(bidentate) ligands for the coordination of metal ions. Treatment of **1** with Ni^{II} or Cu^{II} salts gave two 2:2 (**3**) and four 3:3 (**4**) metallomacrocycles by self-assembly. The structures of the hitherto unknown products were determined by the geometry of the ligands that incorporate either linear or bent spacers between the two binding sites. Complex **3b** is especially interesting due to its two vinyl subunits orientated perpendicular to the plane of the molecule. Complexes **3** and **4** crystallize in planar layers with intercalated solvent molecules (*N*,*N*-dimethylformamide, dimethyl sulfoxide). The molecular structures of five coordination compounds in the solid state have been elucidated by X-ray diffraction.

Introduction

The synthesis of metallomacrocycles by the self-assembly of suitable ligands and metal ions is an important field of current interest in supramolecular coordination chemistry, not only from a structural point of view, but also with respect to molecular containers, catalysis, recognition, and magnetochemistry.[1–3] A large number of literature examples are based on pyridyl or bipyridyl units, which assemble architectures such as triangles, squares, rectangles, polyhedra, and cages.[4–6] Various synthetic approaches to design supramolecular architectures have been discussed by Holliday and Mirkin.[5] The symmetry interaction approach,[7] a method to design metallomacrocycles based on chelating ligands with two or more binding sites, has been widely used by Saalfrank,[8–10] Lehn,[11,12] and Raymond[13] to assemble a variety of macrocyclic systems based on main-group and transition-metal coordination compounds.

We have used this approach to generate new macrocyclic complexes from bis(*N*-acylamidines) **1** as chelating ligands. *N*-Acylamidines **2** are interesting nitrogen-rich monodentate or bidentate ligands for metal-ion coordination.[14–20] Compared to β-imino ketones[21] and β-diimines,[22] the nitrogen atom in the central 3-position alters the electronic structures at the binding sites considerably. Furthermore, conjugation over all five atoms is observed even in the neutral form, and an additional coordination site is offered at the central nitrogen atom. The synthesis of 2:1 *N*-acylamidine/metal complexes was described by Ley and Werner in 1913 as a reaction of the ligands with metal(II) acetates.[23] This reaction yielded neutral 2:1 metal complexes with anionic ligands, the structures of which were proven to be *trans* complexes by Oehme and Pracejus in 1969.[24] The first platinum(II) complex of a chelating *N*-acylamidine has been recently reported.[25] We have previously described several types of metal complexes formed from primary *N*-acylamidines and copper(II) or palladium(II) salts.[14–16] In general, 2:1 metal complexes of **2** have been found to have *trans* or *cis* arrangements (Scheme 1).



Scheme 1. Bis(*N*-acylamidines) **1**, *N*-acylamidines **2**, and 2:1 metal complexes of primary **2** with *cis* and *trans* arrangements of the ligands.

To the best of our knowledge, no examples of 2:2 or 3:3 metallomacrocycles or higher-order assemblies of **1** as ligands have been reported. The coordination geometry of these ligands is expected to be similar to that of bis(β-diketones) or bis(*N*-acylthioureas), which have been synthesized

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[‡] Unsaturated Hetero Chains, XXI. Part XX: Ref.[8]

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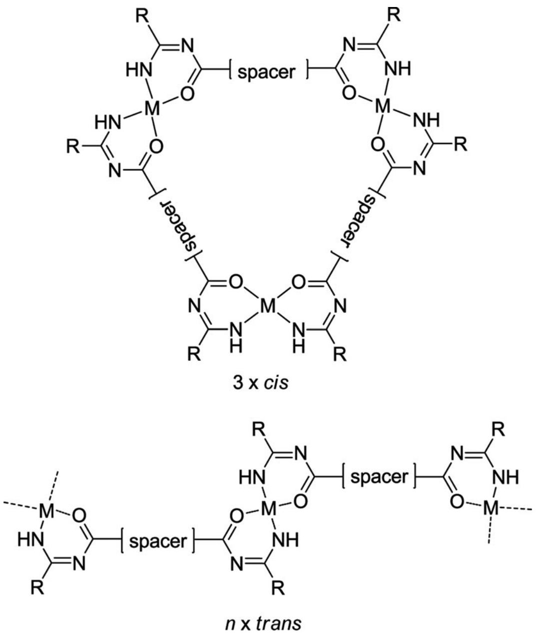
and studied with respect to their coordination behavior by Reedijk et al.,[26] Köhler et al.,[27] Koch et al.,[28,29] and Ugur et al.[30] In this context, we were interested to learn, which types of assemblies were formed by metal complexation of such bis(bidentate) bis(*N*-acylamidines) with bulky, flexible, or rigid spacers of designed geometries. Such ligands have recently been synthesized in our laboratory for the first time.[31,32]

Results and Discussion

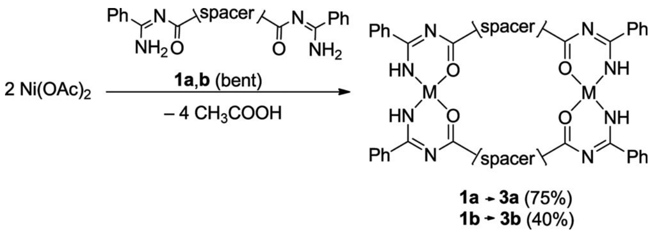
The possibilities for the chelate binding of bis(*N*-acylamidines) **1** in a square-planar coordination environment to give *syn* and *anti* isomers with respect to the spatial orientation of the spacer groups are illustrated in Scheme 2. For *syn* isomers metallomacrocycles, for instance triangles, are expected, whereas *anti* isomers would lead to polymeric chains. Furthermore, the macrocyclic structures will be different if the ligand is not linear but bent, if the coordination sphere is tetrahedral or octahedral, and if the linker has special steric properties. All these possibilities complicate the prediction of the structures of such metal complexes.



Scheme 2. Superstructures arising from *syn* and *anti* arrangements of the coordination sites for bis(*N*-acylamidine)metal complexes.

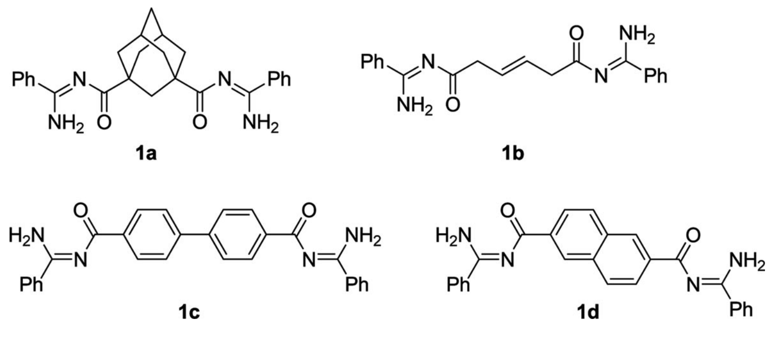
In this work, the coordination behavior of four different primary bis(*N*-acylamidines) **1** towards nickel(II) and copper(II) salts was examined (Scheme 3). The four ligands mainly differ with respect to their coordination geometry: **1a** bears the sterically fixed, bent 1,3-adamantanediyl spacer with a tetrahedral (109.5°) spatial orientation, which allows bis(coordination) in a parallel orientation. Ligand **1b** combines two flexible methylene units with a rigid (*E*)-configured olefinic subunit within the 2-butenediyl spacer. Here, one may expect various types of bis(coordination). Ligand **1c** has a linear biphenyl spacer, which may be subject to internal rotation, and **1d** contains a linear, inflexible 2,5-naphthlenediyl spacer. Ligands **1c** and **1d** allow bis(coordination) in a trigonal-planar (120°) orientation.

Ligands **1a** and **1b** were easily prepared from bis(*N*-acylbenzotriazoles) and *N*-phenylbenzamidine.[31] Ligands **1c** and **1d** were synthesized by using diacyl dichlorides and benzamidine as precursors.[32] The metal complexes (**3** and **4**) of these four ligands were generated by reaction of copper or nickel salts with *cis* coordination within the individual complexes and *syn* orientation with respect to the two binding sites. In general, **1a** and **1b**, with angled spacers, assemble 2:2 metallomacrocycles **3a** and **3b** (Scheme 4), whereas **1c** and **1d**, with linear spacers, led to triangular 3:3 metallomacrocycles **4a–d** (Scheme 5).

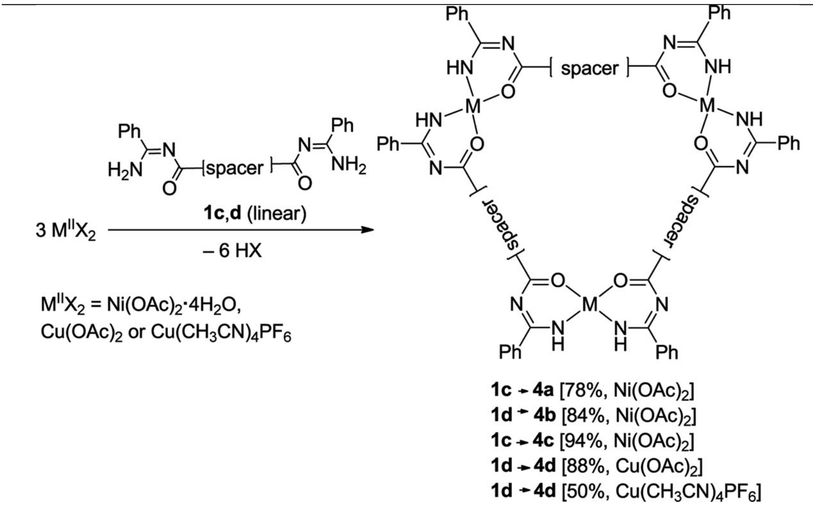


Scheme 4. Self-assembly of 2:2 metallamacrocycles **3a** and **3b** from bent **1a** and **1b** and nickel(II) salts.

In detail, 2:2 metallomacrocycles **3a** and **3b** were synthesized from metal acetates and **1a** and **1b** in *N*,*N*-dimethylformamide (DMF) at 40 °C in moderate to good yields (Scheme 4). Both compounds were crystalline solids, and their molecular structures were obtained by X-ray analysis.



Scheme 3. Bis(*N*-acylamidines) **1a**–**d**.



Scheme 5. Self-assembly of 3:3 metallamacrocycles **4a**–**d** from linear **1c** and **1d** and nickel(II) and copper(II) salts.

In order to generate 3:3 metallomacrocycles **4a**–**d**, 1 equiv. of **1c** or **1d** was treated with 1 equiv. of nickel(II) acetate, copper(II) acetate, or $[Cu^I(CH_3CN)_4]PF_6$ in DMF at 40 °C. In the case of the copper(I) salt, during the reaction copper(I) was oxidized to copper(II), most probably by air, which was not excluded. Four 3:3 metallomacrocycles **4a**–**d** were obtained in good yields (Scheme 5). Metallomacrocycle **4d** was synthesized by two different ways, either by using copper(I) hexafluorophosphate or copper(II) acetate. The latter method gave the product in a higher yield.

These metallomacrocycles are only poorly soluble in polar and nonpolar solvents; thus, ^{1}H and ^{13}C NMR spectra could not be obtained.

Description of the Structures

The crystal structures of **3a**, **3b**, **4a**, **4b**, and **4d** were determined by single-crystal X-ray diffraction. In order to generate crystals suitable for X-ray analysis, it was important to cool DMF or dimethyl sulfoxide (DMSO) solutions of the complexes very slowly to room temperature at a rate of around 10 °C/h without stirring. The crystallization process started at ca. 80 °C. Other crystallization methods are described in the Experimental Section. Many of the crystals contained intercalated solvent molecules (DMF, DMSO), which could not be removed even by prolonged evaporation in vacuo.

Complex **3a** crystallized in the triclinic space group $P\bar{1}$ with one metallomacrocycle in the unit cell together with four molecules of DMSO (Figure 1, Table 1). The two nickel atoms are coordinated by two ligands to form square-planar *cis*-N,O chelates from the deprotonated *N*-acylamidine moieties. Small deviations from ideal square-planar geometry are observed with the Ni^{II} ion 0.009 Å above the plane. The size of the cavity formed is given by the distance between the two face-to-face adamantane units (3.8 Å) and the distance between two oxygen atoms of the same ligand (4.8 Å, Figure 1, right).

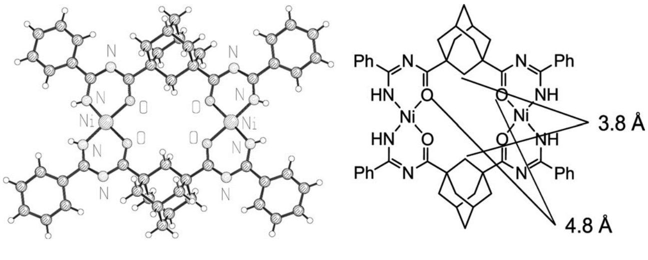


Figure 1. Molecular structure **3a** (left) and internal distances (right).

Table 1. Selected (average) geometrical parameters for **3a**.

Distances [Å]		Angles [°]		Torsional angles [°]	
HN–C	1.303(4)	N–C–N	125.4(3)	N–C–N–C	2.9(6)
HN–C–N	1.353(4)	C–N–C	120.5(3)	C–N–C–O	3.9(6)
HN–C–N–C	1.326(4)	N–C–O	127.9(3)	N–C–O–Ni	2.5(5)
C–O	1.273(3)	C–O–Ni	126.7(2)	C–O–Ni–N	4.2(3)
O–Ni	1.848(2)	O–Ni–N	91.6(1)/176.4(1)	O–Ni–N–C	6.5(3)
Ni–N	1.833(3)	Ni–N–C	127.5(2)	Ni–N–C–N	4.9(6)

Selected bond lengths, bond angles, and torsion angles for **3a** (average of the two six-membered chelate rings), which are also typical for the other Ni^{II} complexes, are listed in Table 1. The O–Ni and N–Ni bond lengths are 1.848(2) and 1.833(3) Å, respectively, which are slightly shorter than those of nickel complexes of neutral *N*-acylamidines as expected. These bond lengths are comparable with 2:2 nickel macrocycles of bis(*N*-acylthioureas) and bis(*N*-acylisoureas).[33] The data reveal the expected electron delocalization within the chelate ring. The shortest Ni–Ni distance is 6.44 Å.

The crystal packing of **3a** (Figure 2) is characterized by a layered structure wherein intercalated DMSO and the metallomacrocycles are stacked on top of each other. Every second DMSO molecule is connected to two amino protons of the metal complex by hydrogen bonding (2.24 and 2.32 Å). The other solvent molecules are located in a layer between two metallomacrocycles (Figure 2, bottom). There is little interaction of the DMSO molecules with the Ni^{II} ions as indicated by the Ni···S distance of 3.75 Å.

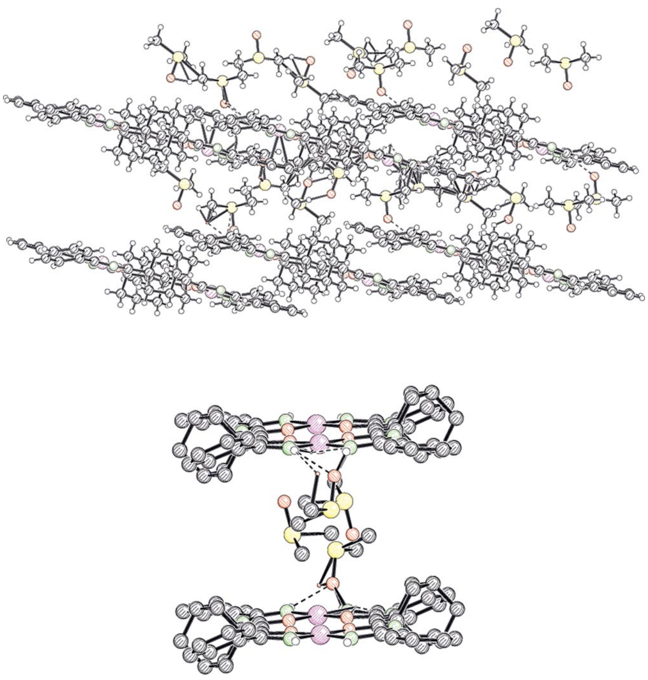


Figure 2. Crystal packing of **3a** (top) and hydrogen bonding between the layers with the intercalating DMSO molecules (bottom). Most hydrogen atoms are omitted for clarity.

Complex **3b** crystallized from the slow diffusion of diethyl ether into a solution of DMF. It crystallized in the monoclinic space group $P2_1/n$ with two metallomacrocycles in every unit cell together with four DMF molecules (Figure 3). Like **3a**, the two four-coordinate nickel ions are bridged by two deprotonated bis(*N*-acylamidines), which results in approximately square-planar bidentate *cis* coordination with the Ni^{II} ion approximately 0.004 Å above the plane. Interestingly, with respect to the geometry of the 2-butene-1,4-diyl spacer unit, the two olefin groups of the two ligands are orientated exactly parallel to each other (Figure 3, left) with the π orbitals arranged perpendicular to the plane of the macrocycle, which suggests an additional possibility for coordination inside the metallomacrocycle, e.g. for late-transition metal ions. Thus, **1b** unexpectedly shows the same complexation behavior as **1a**, which has a bent adamantane-1,3-diyl spacer, with the ability to position the coordination sites in a parallel fashion. The distances between the opposing olefinic carbon atoms is 6.6 Å and that of the two oxygen atoms is 5.7 Å.

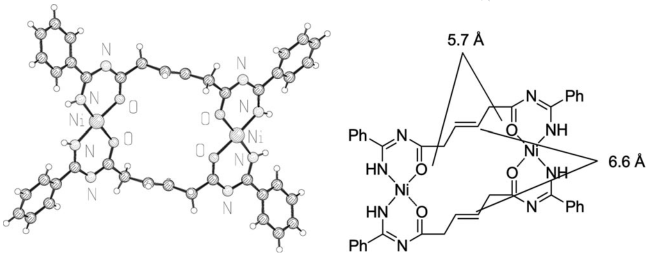


Figure 3. Molecular structure of **3b** (left) and internal distances (right).

The crystal lattice of **3b** is characterized by separate layers of the macrocycles, which are interconnected by DMF molecules (Figure 4, bottom). Thus, the oxygen atoms of the DMF molecules are hydrogen-bonded to two *cis*-NH groups of the chelates (NH···O 2.17 and 2.22 Å) and to the oxygen atoms of the chelate of the next layer by the DMF CH group [O···CH(DMF) 2.42 Å]. The crystal packing (Figure 4, bottom) shows two different layers of metallomacrocycles stacked on top of each other with the shortest Ni–Ni distance of 3.60 Å. The second layer completely covers the cavity between two layers of the same arrangement. Therefore, no channels were observed in the crystal structure. The structural parameters for the six-membered chelate rings are similar to those of **3b**.

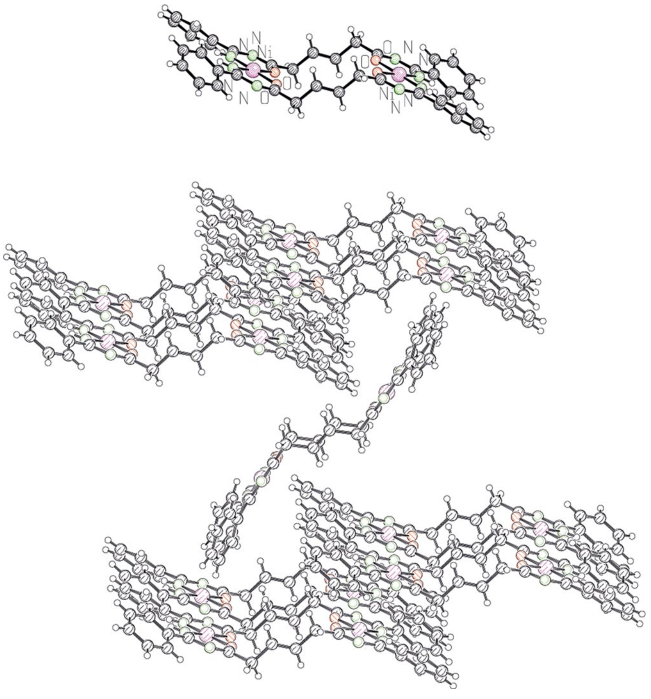


Figure 4. Another view of the molecular structure of **3b** (top) and crystal packing (bottom). Solvent molecules are omitted for clarity.

Complex **4a** (Figure 5) crystallizes in the triclinic space group $P\bar{1}$ with four metallomacrocycles in the unit cell together with 32 DMSO molecules. The three nickel ions are connected to three anionic *N*-acylamidine ligands in a square-planar *cis*-N,O chelate coordination. A minor deviation from ideal square-planar geometry is observed as the chelate rings are slightly twisted. The size of the internal cavity of the metallomacrocycle measured between the aromatic protons of the spacer unit is 6.3 and 6.9 Å (Figure 5, right). The biphenyl spacer units are almost coplanar with the coordination sphere of the nickel atoms but display a torsion angle within the biphenyl system of about 30°. The planar macrocycles crystallize to form layers with an approximate distance of 3.6–3.8 Å. The bond lengths and

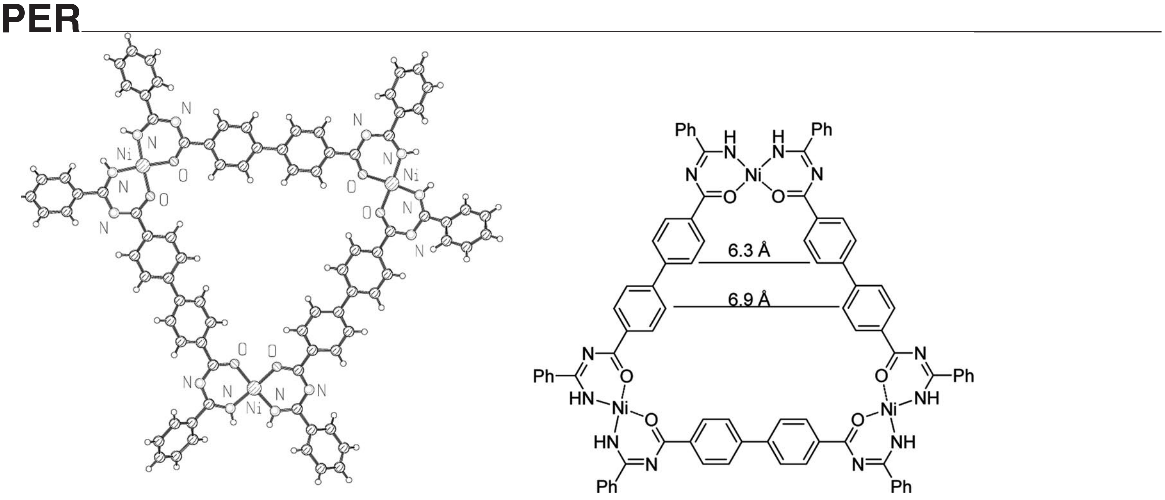


Figure 5. Molecular structure of **4a** (left) and internal distances (right).

angles resemble those of 2:2 nickel macrocycles of bis(*N*-acylamidines) and are comparable to 3:3 nickel macrocycles of bis(*N*-acylthioureas) with phenyl spacer units.[27]

Complex **4b** crystallized in the trigonal space group $R\bar{3}$ with six metallomacrocycles per unit cell together with 18 DMSO molecules (Figure 6). The structural properties of this C_3-symmetrical complex are similar to those of **4a**. Square-planar coordination spheres of the nickel atoms were found. The average N–Ni–O angle is 91.2(1)°, which leads to a small deviation from ideal square-planar geometry with the nickel atom approximately 0.019 Å above the plane. This is also indicated by the torsion angles within the chelate ring system, which are between 1.6(8) and 8.2(8)° and show substantial deviations from the ideal planar chelate ring system compared to **4a**, where all of the torsion angles are less than 5(6)°. The shortest distance between the aromatic protons of the two different ligands in the inside of the metallomacrocycle is 4.5 Å (Figure 6, right).

The naphthalene units are coplanar with the nickel coordination spheres, whereas the phenyl substituents of the *N*-acylamidines are tilted [–21.1(6) and –40.9(6)°]. Three of the DMSO molecules are connected to the macrocycle by hydrogen bonds to each two of the NH groups of the chelates (NH···O 2.16 and 2.44 Å). Similar to **4a**, **4b** crystallizes to form layers with distances of approximately 3.8 Å.

The magnetic properties of **4b** in the solid state were measured in the temperature range of 3–300 K. The compound is essentially diamagnetic, which indicates that there is no significant interaction of the interlayer DMSO molecules with the nickel(II) ions. On the basis of these measurements, the nickel(II) ions can be described as square-planar.[34]

Crystals of **4d** suitable for X-ray analysis were obtained from $[Cu(CH_3CN)_4]PF_6$ and **1d** but not from Cu^{II} salts. The reactants were stirred in DMF in the presence of air so that the copper(I) salt was oxidized. The slightly yellow solution slowly turned blue on formation of copper(II). Slow diffusion of diethyl ether into the solution led to red crystals of **4d**. Complex **4d** crystallized in the triclinic space group $P\bar{1}$ with two metallomacrocycles in the unit cell together with a minimum of six molecules of DMF. Due to the presence of these solvent molecules, the structure could not be refined with high precision (R_1 = 0.1011, Figure 7). The three copper atoms are interconnected by three deproton-

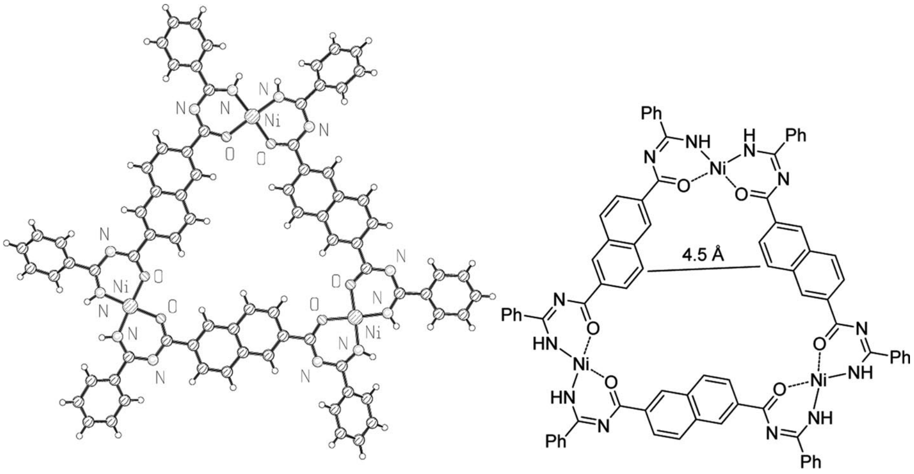


Figure 6. Molecular structure of **4b** (left) and internal distances (right).

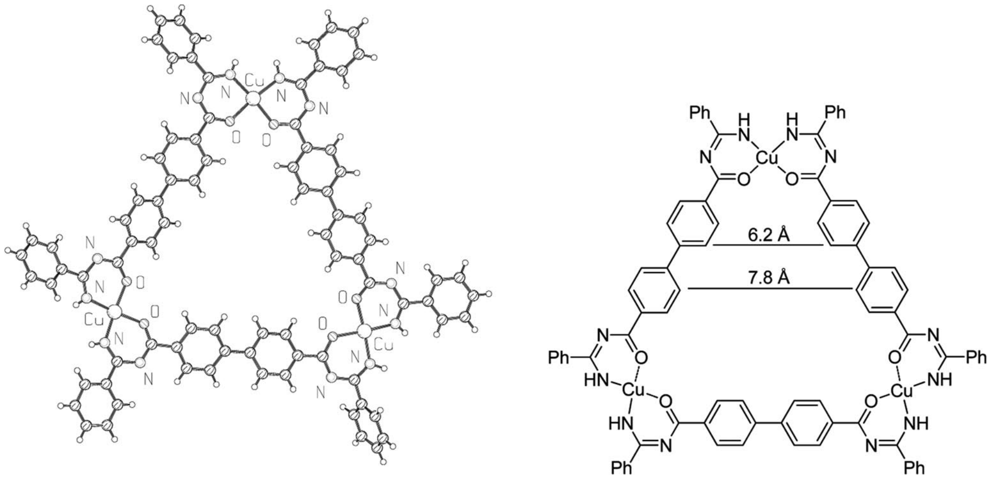


Figure 7. Molecular structure of **4d** (left) and internal distances (right).

ated *N*-acylamidine ligands in a square-planar *cis*-N,O coordination. Again, we observed small deviations from the ideal square-planar geometry, as the Cu^{II} ion is located 0.047 Å below the plane of the complex.

The internal distances of the metallomacrocycle are 6.2 and 7.8 Å, measured between the aromatic protons of the spacer unit (Figure 7, right). The biphenyl spacer units are almost coplanar with the coordination sphere of the copper atoms but are tilted by about 25° within the biphenyl system. The average O–Cu and N–Cu bond lengths are 1.918(3) and 1.919(3) Å, respectively, which are slightly longer than those of **4a** as expected. The bond lengths of the *N*-acylamidine moieties reveal the expected electron delocalization within the chelate rings.

Conclusions

We have demonstrated that the bis(bidentate) bis(*N*-acylamidines) **1**, which incorporate various spacer units, are well suited for the preparation of supramolecular architectures by self-assembly. We obtained two 2:2 metallomacrocycles (**3a** and **3b**) from the bent **1a** and **1b**. The structure of **3b** is surprising, as – in spite of the (*E*) configuration of the alkenyl moieties – the two π bonds are located perpendicular to the molecular plane, which creates a cavity with internal π-donor properties. Furthermore, four 3:3 metallomacrocycles **4a**–**d** were obtained, which are characterized by planar structures and often crystallized in layers with intercalated solvent molecules (DMF, DMSO). Further work directed towards the synthesis of 3D coordination compounds based on *N*-acylamidine ligands is underway.

Experimental Section

Materials and Methods: IR spectra were recorded with a Varian 3100 FTIR spectrometer by using a Specac Golden Gate Single Reflection ATR sampling system. MALDI MS data were recorded with Lazarus IIIDE (Organic Institut, Münster) or Reflex IV (Bruker Daltonics, Bremen) instruments by using an N_2 laser, 337 nm, 3 ns. CHN elemental analysis was performed with a Elementar Vario El III apparatus.

General Procedure (GP) for the Synthesis of 3a and 4a–d: A solution of metal acetate (0.1 mmol) in DMF (2 mL) was stirred at 40 °C until the metal salt had dissolved. The ligand (0.1 mmol) dissolved in DMF (2 mL) at 40 °C was added dropwise over 10 min, and the mixture was stirred at 40 °C for 30 min. The metal complex precipitated immediately or on cooling to room temperature. The solid was collected by filtration and washed with a small amount of DMF. The products were purified as stated below.

***cis*-[Ni{(1a–2H)-*N,O*}]$_2$ (3a):** Adamantane-1,3-dicarboxylic acid bis(1-amino-1-phenylmethylideneamide) (**1a**, 42.8 mg (0.100 mmol) and $Ni(OAc)_2\cdot 4H_2O$ (24.7 mg, 0.100 mmol) were treated according to the GP. Recrystallization from DMSO gave orange crystals. Yield: 36.2 mg (0.037 mmol, 75%). M.p. >300 °C. IR (ATR): $\tilde{\nu}$ = 3069 (vw), 2932 (w), 2903 (m), 2853 (w), 1591 (m), 1545 (s), 1479 (m), 1452 (s), 1429 (m), 1414 (m), 1377 (s), 1350 (m), 1325 (m), 1308 (s), 1258 (m), 1240 (m), 1140 (w), 1103 (w), 1030 (w), 1003 (w), 957 (w), 918 (w), 793 (w), 758 (w), 704 (s), 685 (vs) cm^{-1}. MS (MALDI, matrix DCTB {*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile}): *m*/*z* = 969–976 $[C_{52}H_{52}N_8Ni_2O_4 + H]^+$. $C_{52}H_{52}N_8Ni_2O_4$ (970.4): calcd. C 64.36, H 5.40, N 11.55; found C 64.11, H 5.38, N 11.52.

X-ray Crystal Structure Analysis of 3a:[35] $C_{52}H_{52}N_8Ni_2O_4\cdot 4C_2H_6OS$, M = 1282.95, orange crystal, 0.40 × 0.15 × 0.07 mm, a = 10.4056(4), b = 12.3064(7), c = 13.0618(4) Å, α = 64.856(3), β = 83.375(3), γ = 86.827(2)°, V = 1503.99(11) Å^3, $\rho_{\text{calcd.}}$ = 1.416 g cm^{-3}, μ = 0.826 mm^{-1}, empirical absorption correction (0.734 ≤ T ≤ 0.944), Z = 1, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 17245 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 Å^{-1}, 7092 independent (R_{int} = 0.064) and 4484 observed reflections [$I \geq 2\sigma(I)$], 380 refined parameters, R = 0.061, wR^2 = 0.177, max. (min.) residual electron density 0.72 (–1.07) e Å^{-3}, hydrogen atoms at N1 found from difference fourier calculations, others calculated and refined as riding atoms.

***cis*-[Ni{(1b–2H)-*N,O*}]$_2$ (3b):** A solution of $Ni(OAc)_2\cdot 4H_2O$ (24.7 mg, 0.100 mmol) in DMF (2 mL) was stirred at 40 °C until the metal salt had dissolved. (*E*)-Hex-3-enedioic acid bis(1-amino-1-phenylmethylideneamide) (**1b**, 34.8 mg, 0.100 mmol) dissolved in DMF (2 mL) at 40 °C was added dropwise to the metal salt solution over 10 min, and the mixture was stirred for 30 min. Slow diffusion of diethyl ether (5 mL) into the DMF solution led to red crystals of **3b** within a week. The crystals were collected by filtration and dried under vacuum. Yield: 16.6 mg (0.020 mmol, 40%). M.p. 140 °C (decomposition). IR (ATR): $\tilde{\nu}$ = 3217 (w), 2930 (vw), 1653 (m), 1553 (s), 1408 (vs), 1342 (m), 1256 (w), 1101 (w), 1049 (w), 1028 (w), 926 (w), 824 (w), 779 (m), 754 (w), 737 (w), 675 (s), 665 (s), 615 (s) cm^{-1}. MS (MALDI): *m*/*z* = 809.1 $[C_{40}H_{36}N_8Ni_2O_4 + H]^+$.

X-ray Crystal Structure Analysis of 3b:[35] $C_{40}H_{36}N_8Ni_2O_4\cdot 2C_3H_7NO$, $M = 956.38$, orange crystal, 0.35 × 0.25 × 0.03 mm, a = 10.5711(2), b = 16.8185(3), c = 15.5769(2) Å, β = 90.504(1)°, V = 2769.31(8) Å^3, $\rho_{\text{calcd.}}$ = 1.147 g cm^{-3}, μ = 0.729 mm^{-1}, empirical absorption correction ($0.785 \leq T \leq 0.979$), $Z = 2$, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 20639 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 6462 independent (R_{int} = 0.046) and 5410 observed reflections [$I \geq 2\sigma(I)$], 297 refined parameters, R = 0.059, wR^2 = 0.183, max. (min.) residual electron density 0.57 (–0.52) e Å^{-3}; other solvents (probably diethyl ether) could not be refined in a chemically meaningful way, therefore, the SQUEEZE routine was used, hydrogen atoms at N1 and N12 were found from difference fourier calculations, others were calculated and refined as riding atoms.

***cis*-[Ni{(1c–2H)-*N*,*O*}]$_3$ (4a):** Biphenyl-4,4′-dicarboxylic acid bis(1-amino-1-phenylmethylideneamide) (**1c**, 44.6 mg,0.100 mmol) and $Ni(OAc)_2\cdot 4H_2O$ (24.7 mg, 0.100 mmol) were treated according to the GP. In order to obtain crystals, the solid was recrystallized from DMSO to give orange crystals. Yield: 45.5 mg (0.028 mmol, 84%). M.p. > 300 °C. IR (ATR): $\tilde{\nu}$ = 3304 (w), 3061 (w), 1607 (vw), 1589 (w), 1566 (m), 1533 (m), 1495 (w), 1452 (m), 1423 (s), 1404 (m), 1369 (vs), 1302 (m), 1271 (m), 1246 (m), 1180 (m), 1157 (m), 1057 (w), 1028 (m), 1003 (m), 847 (m), 810 (m), 795 (m), 756 (s), 704 (vs), 644 (m), 629 (m) cm^{-1}. MS (MALDI): *m*/*z* = 1509.3 $[C_{84}H_{60}N_{12}Ni_3O_6 + H]^+$. $C_{84}H_{60}N_{12}Ni_3O_6$ + 1.5 DMSO (1626.7): calcd. C 64.23, H 4.28, N 10.33; found C 64.25, H 4.21, N 10.54.

X-ray Crystal Structure Analysis of 4a:[35] $C_{84}H_{60}N_{12}Ni_3O_6\cdot 8C_2H_6OS$, $M = 2134.59$, orange crystal, 0.40 × 0.30 × 0.05 mm, a = 15.5954(2), b = 22.4297(3), c = 30.5163(5) Å, α = 91.203(1), β = 93.253(1), γ = 102.921(2)°, V = 10381.3(3) Å^3, $\rho_{\text{calcd.}}$ = 1.366 g cm^{-3}, μ = 0.766 mm^{-1}, empirical absorption correction ($0.749 \leq T \leq 0.963$), $Z = 4$, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 58596 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.59 Å^{-1}, 35585 independent (R_{int} = 0.069) and 24804 observed reflections [$I \geq 2\sigma(I)$], 2499 refined parameters, R = 0.123, wR^2 = 0.330, max. (min.) residual electron density 3.61 (–2.46) e Å^{-3}; hydrogen atoms were calculated and refined as riding atoms, solvent molecules were refined with geometrical and thermal restraints, weakly diffracting crystals of poor quality.

***cis*-[Ni{(1d–2H)-*N*,*O*}]$_3$ (4b):** Naphthalene-2,6-dicarboxylic acid bis(1-amino-1-phenylmethylideneamide) (**1d**, 42.0 mg 0.100 mmol) and $Ni(OAc)_2\cdot 4H_2O$ (24.7 mg, 0.100 mmol) were treated according to the GP. In order to obtain crystals suitable for X-ray analysis, the solid was recrystallized from DMSO to give orange crystals. Yield: 37.0 mg (0.026 mmol, 78%). M.p. >300 °C. IR (ATR): $\tilde{\nu}$ = 3059 (vw), 3026 (vw), 1601 (vw), 1587 (w), 1537 (s), 1456 (m), 1425 (m), 1391 (s), 1354 (s), 1261 (m), 1242 (m), 1200 (m), 1184 (m), 1146 (w), 1117 (m), 1051 (w), 1028 (w), 1001 (w), 966 (w), 918 (m), 822 (w), 770 (s), 691 (vs) cm^{-1}. MS (MALDI, matrix DCTB): *m*/*z* = 1429–1431 $[C_{78}H_{54}N_{12}Ni_3O_6 + H]^+$. $C_{78}H_{54}N_{12}Ni_3O_6$ (1431.4): calcd. C 65.45, H 3.80, N 11.74; found C 64.93, H 3.89, N 11.67.

X-ray Crystal Structure Analysis of 4b:[35] $C_{78}H_{54}N_{12}Ni_3O_6\cdot 3C_2H_6OS$, $M = 1665.85$, orange crystal, 0.15 × 0.12 × 0.03 mm, a = 26.2897(4), c = 19.8066(4) Å, V = 11855.3(3) Å^3, $\rho_{\text{calcd.}}$ = 1.400 g cm^{-3}, μ = 0.853 mm^{-1}, empirical absorption correction ($0.883 \leq T \leq 0.975$), $Z = 6$, trigonal, space group $R\bar{3}$ (No. 148), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 18683 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 6280 independent (R_{int} = 0.050) and 4664 observed reflections [$I \geq 2\sigma(I)$], 342 refined parameters, R = 0.0601, wR^2 = 0.136, max. (min.) residual electron density 0.94 (–0.37) e Å^{-3}; hydrogen atoms at N1 and N18 were found from difference fourier calculations, others were calculated and refined as riding atoms.

***cis*-[Cu{(1d–2H)-*N*,*O*}]$_3$ (4c):** Naphthalene-2,6-dicarboxylic acid bis(1-amino-1-phenylmethylideneamide) (**1d**, 42.0 mg, 0.100 mmol) and $Cu(OAc)_2$ (18.1 mg, 0.100 mmol) were treated according to the GP. The precipitate was collected by filtration and washed with DMF (2 mL), toluene (2 mL), and pentane (2 mL) to give a brown solid. Yield: 45.3 mg (0.031 mmol, 94%). M.p. >300 °C. IR (ATR): $\tilde{\nu}$ = 3325 (w), 3267 (w), 3065 (vw), 2922 (vw), 2884 (vw), 1665 (m), 1589 (w), 1543 (s), 1470 (m), 1454 (s), 1422 (s), 1383 (s), 1350 (vs), 1256 (m), 1234 (m), 1198 (m), 1188 (m), 1115 (m), 1092 (m), 1055 (m), 1028 (m), 1001 (w), 924 (m), 827 (m), 797 (m), 762 (vs), 689 (s), 660 (m) cm^{-1}. MS (MALDI, matrix DCTB): *m*/*z* = 1443–1450 $[C_{78}H_{54}N_{12}Cu_3O_6 + H]^+$. $C_{78}H_{54}N_{12}Cu_3O_6$ (1446.0): calcd. C 64.79, H 3.76, N 11.62; found C 64.38, H 3.76, N 11.58.

***cis*-[Cu{(1c–2H)-*N*,*O*}]$_3$ (4d). Method 1:** Ligand **1c** (44.6 mg, 0.100 mmol) and $Cu(OAc)_2$ (18.1 mg, 0.100 mmol) were treated according to the GP. The precipitate was collected by filtration and washed with DMF (2 mL), toluene (2 mL), and pentane (2 mL). Yield: 45.1 mg (0.029 mmol, 88%). **Method 2:** Ligand **1c** (44.6 mg, 0.100 mmol) was dissolved in DMF (1 mL) and added dropwise to a solution of $[Cu(CH_3CN)_4]PF_6$ (37.2 mg, 0.100 mmol) in DMF (1 mL). On stirring for 15 min, the solution slowly turned blue due to the formation of copper(II). Slow diffusion of diethyl ether into the solution led to red crystals of **4d** within a week. The crystals were collected by filtration and dried under vacuum. Yield: 26.0 mg (0.017 mmol, 50%). M.p. >300 °C. IR (ATR): $\tilde{\nu}$ = 3314 (vw), 3063 (vw), 2926 (vw), 2870 (vw), 1661 (m), 1589 (m), 1568 (m), 1535 (s), 1495 (m), 1454 (s), 1425 (s), 1406 (m), 1366 (vs), 1256 (m), 1231 (m), 1180 (m), 1155 (m), 1096 (m), 1028 (w), 1003 (m), 934 (w), 851 (m), 795 (m), 754 (s), 745 (m), 708 (s), 660 (m) cm^{-1}. MS (MALDI, matrix DCTB): *m*/*z* = 1546–1550 $[C_{84}H_{60}N_{12}Cu_3O_6 + Na]^+$. $C_{84}H_{60}Cu_3N_{12}O_6$ + 0.5 DMF (1557.8): calcd. C 65.80, H 4.10, N 11.22; found C 65.64, H 4.04, N 10.97.

X-ray Crystal Structure Analysis of 4d:[35] $C_{84}H_{60}Cu_3N_{12}O_6\cdot 3C_3H_7NO$, $M = 1743.35$, red crystal, 0.40 × 0.35 × 0.10 mm, a = 13.3524(2), b = 13.4896(3), c = 25.5935(6) Å, α = 79.232(1), β = 76.486(1), γ = 79.531(1)°, V = 4357.08(16) Å^3, $\rho_{\text{calcd.}}$ = 1.329 g cm^{-3}, μ = 0.792 mm^{-1}, empirical absorption correction ($0.742 \leq T \leq 0.925$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 58467 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 20282 independent (R_{int} = 0.071) and 14756 observed reflections [$I \geq 2\sigma(I)$], 1118 refined parameters, R = 0.075, wR^2 = 0.210, max. (min.) residual electron density 1.14 (–0.89) e Å^{-3}; other solvents could not be identified in a chemically meaningful way, therefore the SQUEEZE routine was used, hydrogen atoms at N1 were found from difference fourier calculations, others were calculated and refined as riding atoms, some phenyl groups show disorder (refined for C12E–C17E).

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[34] Above 270 K, the thermal variation of the molar susceptibility exceeds the value of the product $\chi_M T = 0.375\,\mathrm{emu\,K\,mol^{-1}}$. With regard to the number of three nickel(II) atoms per molecule, we interpret this observation by the presence of a small amount of a paramagnetic impurity.

[35] Data sets were collected with Nonius KappaCCD diffractometers, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B. V., **1998**), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326), absorption correction SORTAV (R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421–426) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr., Sect. A* **2003**, *59*, 228–234), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473), structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122), graphics SCHAKAL (E. Keller, University of Freiburg, **1997**). CCDC-854332 (for **3a**), -854333 (for **3b**), -854334 (for **4a**), -854335 (for **4b**), and -854336 (for **4d**) 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.

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