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Zinc(II), Copper(II), and Nickel(II) Complexes of Bis(tripodal) Diamide Ligands – Reversible Switching of the Amide Coordination Mode upon Deprotonation

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A series of dinuclear Zn(II), Cu(II) and Ni(II) complexes of two new bis-tripodal ligands with aromatic (H_2-**4a**) and aliphatic (H_2-**4b**) diamide spacers has been synthesized and structurally characterized. Each of the two tripodal entities of the neutral dinucleating ligands coordinates to one metal ion via three amine functions and a carbonyl oxygen atom of the amide groups. Either trifluoroacetate counterions or solvent molecules complete the trigonal-bipyramidal (Zn, **5a**), square-pyramidal (Cu, **6a** and **6b**), and octahedral (Ni, **7a** and **7b**) coordination environment at the metal centers. Complexes **5a**, **6a**, and **7a** with the phenylene-bridged diamide ligand are readily deprotonated by potassium *tert*-butoxide effecting a rearrangement of the dinuclear complexes. In the resulting zinc and copper complexes **8** and **9**, one of the metal centers is coordinated by three amine functions of a tripodal subunit and the two amidate nitrogen atoms of the deprotonated ligand **4a**$^{2-}$ while the coordination geometry of the second metal atom remains unchanged. The analogous nickel compound crystallizes as neutral tetranuclear complex (**10**)$_2$ with intermolecular coordination of two amide carbonyl oxygen atoms to the nickel atoms of an adjacent dinuclear complex. The resulting coordination mode with binding of all four donor functions of the diamide spacer to three discrete metal centers is to date unprecedented for *ortho*-phenylene-bridged acetamides. The rearrangement upon deprotonation has been shown to be fully reversible and the starting complexes can be retrieved upon protonation of the two amidate functions. Synthesis of the trinuclear zinc complex **11** with coordination of the two amidate nitrogen atoms to a third metal center was achieved via deprotonation of (H_6-**4a**)(CF_3CO_2)$_4$ by three equivalents of diethylzinc. In protic solvents **11** rapidly rearranges to give the entropically favored dinuclear complex **8** with elimination of one equivalent of zinc trifluoroacetate.

Introduction

Carboxamides are not only ubiquitous in the biosphere as essential parts of proteins, but they are also versatile and interesting ligands in synthetic coordination chemistry. Neutral amides exclusively coordinate to metal ions via the lone pair at the carbonyl oxygen atom, as the lone pair at the nitrogen is delocalized over the whole amide group and, consequently, not available for metal coordination. On the other hand, deprotonated amides preferably coordinate to metal ions via their amidate nitrogen atom.[1]

Due to the presence of N-donor functions in many naturally occurring metalloproteins, ligands combining amide and pyridine donor groups have been intensively investigated.[2] A well-known group of these ligands are bis(pyridine-2-carboxamides), consisting of two carboxamide units connected by a suitable amide-N-bridging group, mostly an *ortho*-phenylene[3,4] or ethylene[3,5] spacer. Analogous ligands with aliphatic amine functions instead of the pyridine rings are also known.[6]

These ligands are readily deprotonated and usually bind to metal ions with two amidate and two additional nitrogen donors, often providing an essentially planar donor environment. For the *ortho*-phenylene-bridged ligand type, the deprotonated diamide can act to some degree as an anionic analog of *ortho*-phenanthroline.

Alsfasser et al. have synthesized a series of tetradentate tripodal ligands with amide donor groups by attaching different amino acids or small peptide chains to a bis(2-pyridylmethyl)amine unit. The neutral ligands coordinate to zinc(II), copper(II) and nickel(II) with the pyridyl donor functions, the tertiary amine, and the amide carbonyl oxygen atom.[7] For selected zinc(II) complexes, a rearrangement of the ligand with coordination of the amidate nitrogen atom was observed upon deprotonation. This switching of the amide coordination mode has been to be fully reversible upon protonation with hydrochloric acid.[8] Similar pH-dependent rearrangements have been reported by other groups for complexes with tripodal ligands featuring amine and amide donor groups.[9]

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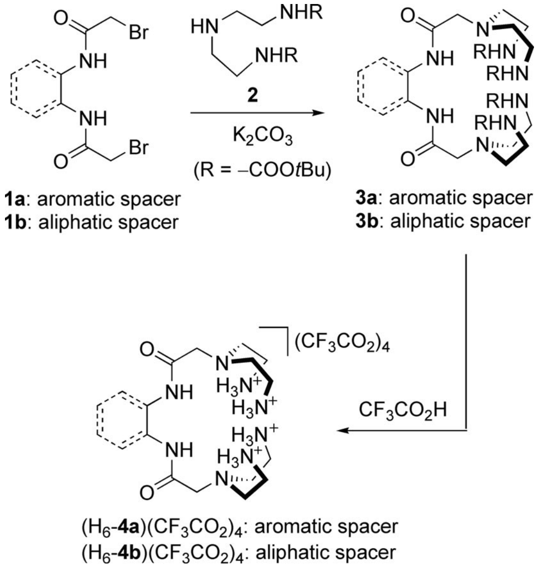
Compared to their analogs with aromatic pyridyl donor groups, tripodal ligands with aliphatic amine groups have attracted much less attention. Due to their higher flexibility, the aliphatic ligands exhibit a more variable coordination behavior toward metal ions. The influence of the ligand arm lengths on the coordination geometry of the copper(II)[10] and nickel(II)[11] complexes with a series of symmetric and unsymmetric aliphatic tetraamine ligands has been studied.

Herein we report on the synthesis and characterization of two new protonated bis(tripodal) ligands (H_6-**4a**)($CF_3CO_2)_4$ and (H_6-**4b**)($CF_3CO_2)_4$ (Scheme 1) featuring the two adjacent amide groups of bis(pyridinecarboxamides) linked to two tridentate aliphatic triamines. The coordination chemistry of the neutral deprotonated ligands with zinc(II), copper(II), and nickel(II) will be described in addition to the unusual behaviour observed for the complexes with the *o*-phenylene-bridged ligand upon further deprotonation. .

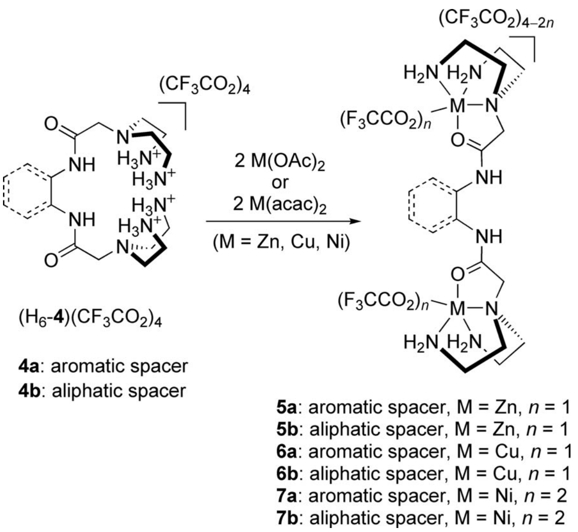


Scheme 1. Synthesis of the bis(tripodal) trifluoroacetate salts (H_6-**4**)($CF_3CO_2)_4$ with aromatic and aliphatic spacers.

Results and Discussion

The protonated diamide ligands of type (H_6-**4**)($CF_3CO_2)_4$ were synthesized by substitution of the bromides in compounds of type **1** under basic conditions with amine **2**, bearing *tert*-butoxycarbonyl (Boc) protecting groups at its primary amine functions (Scheme 1). This reaction yields the Boc-protected diamides of type **3**. Subsequent removal of the Boc-protecting groups by treatment with trifluoroacetic acid leads to precipitation of the tetraprotonated trifluoroacetate salts (H_6-**4**)($CF_3CO_2)_4$. The molecular structure of (H_6-**4a**)($CF_3CO_2)_4$ has been determined and is described in the Supporting Information. The neutral diamide ligands of type H_2-**4** could not be isolated, as an intramolecular attack of the primary amine functions at the carbonyl groups occurs upon deprotonation, resulting in the decomposition of the ligand by elimination of the bridging diamine.

The dinuclear zinc(II), copper(II), and nickel(II) complexes **5**, **6**, and **7** of the neutral ligands H_2-**4** were obtained via in situ deprotonation of the trifluoroacetate salts (H_6-**4**)($CF_3CO_2)_4$ by acetate or acetylacetonate ligands of the metal precursors (Scheme 2). Decomposition of the ligand upon deprotonation was not observed under these conditions, as coordination of the generated primary amine functions to the transition metal ion prevents the intramolecular attack at the carbonyl group. Complexes of types **5**, **6**, and **7** have been obtained in good yields with the higher yields found for the complexes bearing ligand H_2-**4a** with the aromatic spacer. Crystals of **5a**·MeOH, **6a**·MeOH, **6b**·2DMF, **7a**$(MeOH)_2$·0.5MeOH, and **7b**·2MeCN suitable for X-ray diffraction analyses were obtained by slow diffusion of diethyl ether into a solution of the complexes in either methanol, acetonitrile, or DMF.



Scheme 2. Synthesis of the symmetric dinuclear complexes of types **5**, **6**, and **7** bearing the neutral diamide ligands H_2-**4a** and H_2-**4b**.

The X-ray structure analyses for complexes of types **5**–**7** (see Figures 1, 2, and 3) show each of the metal centers coordinated by the three amine donors and the carbonyl oxygen atom of the tripodal entities. In the solid state, the coordination spheres of the metals are completed by one (Zn, Cu) or two (Ni) trifluoroacetate counterions with the exception of **7a**$(MeOH)_2$·0.5MeOH, where only one trifluoroacetato anion coordinates to each metal center in addition to one methanol molecule. The observation of only one set of signals for the counterions in the ^{13}C NMR spectrum of the zinc complexes **5a** and **5b** indicates the facile displacement of the coordinated trifluoroacetato ions in solution.

The structure analysis of complex **5a**·MeOH reveals a trigonal-bipyramidal coordination environment for both metal centers [$\tau^{[12]} = 0.73$ (Zn1) and $\tau = 0.96$ (Zn2)]. The axial positions are occupied by the tertiary amine function and a trifluoroacetato ligand. The Zn–N_{tert} distances [Zn1–

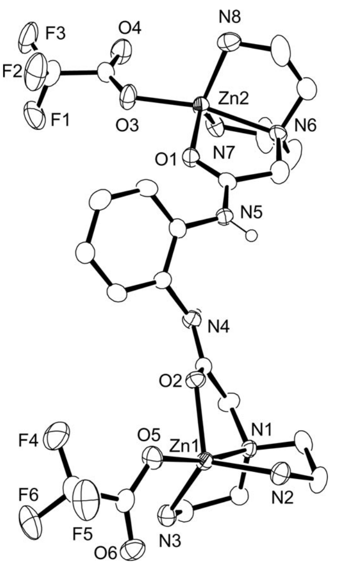


Figure 1. Molecular structures of the complex cation in **5a**·MeOH (uncoordinated counterions and hydrogen atoms except amide N–H protons are omitted for clarity). Selected bond lengths [Å] and angles [°]: Zn1–O2 2.065(2), Zn1–O5 1.997(3), Zn1–N1 2.241(3), Zn1–N2 2.052(3), Zn1–N3 2.043(4), Zn2–O1 2.053(2), Zn2–O3 2.008(3), Zn2–N6 2.257(3), Zn2–N7 2.034(4), Zn2–N8 2.025(4); N1–Zn1–O5 166.84(11), N1–Zn1–O2 77.53(10), N1–Zn1–N2 83.21(13), N1–Zn1–N3 81.32(12), O2–Zn1–N2 107.74(14), O2–Zn1–N3 121.23(13), N2–Zn1–N3 123.3(2), N6–Zn2–O3 164.45(11), N6–Zn2–O1 77.98(10), N6–Zn2–N7 82.59(14), N6–Zn2–N8 88.84(14), O1–Zn2–N7 123.26(15), O1–Zn2–N8 109.19(14), N7–Zn2–N8 120.5(2).

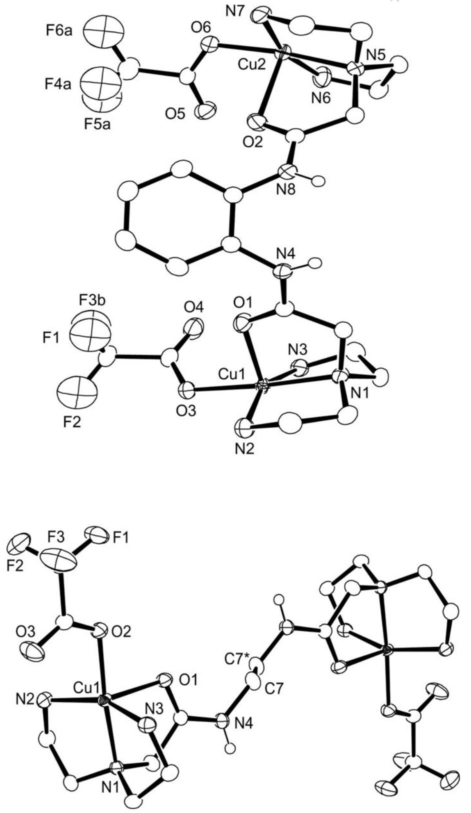


Figure 2. Molecular structures of the complex cations in **6a**·MeOH (top) and **6b**·2DMF (bottom, uncoordinated counterions and hydrogen atoms except amide N–H protons are omitted for clarity). Selected bond lengths [Å] and angles [°] for **6a**·MeOH: Cu1–O1 2.336(3), Cu1–O3 1.979(3), Cu1–N1 2.072(4), Cu1–N2 2.004(4), Cu1–N3 1.980(4), Cu2–O2 2.218(3), Cu2–O6 1.980(3), Cu2–N5 2.070(3), Cu2–N6 2.007(4), Cu2–N7 1.981(3); O1–Cu1–O3 92.90(12), O1–Cu1–N1 78.61(12), O1–Cu1–N2 94.43(13), O1–Cu1–N3 96.28(15), O3–Cu1–N1 170.98(14), O3–Cu1–N2 92.41(14), O3–Cu1–N3 99.25(15), N1–Cu1–N2 85.26(15), N1–Cu1–N3 84.9(2), N2–Cu1–N3 163.7(2), O2–Cu2–O6 93.06(12), O2–Cu2–N5 80.35(12), O2–Cu2–N6 93.21(14), O2–Cu2–N7 108.16(14), O6–Cu2–N5 173.14(13), O6–Cu2–N6 92.36(13), O6–Cu2–N7 98.05(13), N5–Cu2–N6 86.13(13), N5–Cu2–N7 85.92(13), N6–Cu2–N7 155.55(15). Selected bond lengths [Å] and angles [°] for **6b**·2DMF: Cu1–O1 2.2585(10), Cu1–O2 1.9683(10), Cu1–N1 2.0667(11), Cu1–N2 1.9972(13), Cu1–N3 1.9936(13); O1–Cu1–O2 93.16(4), O1–Cu1–N1 80.38(4), O1–Cu1–N2 110.15(5), O1–Cu1–N3 95.60(5), O2–Cu1–N1 173.53(4), O2–Cu1–N2 96.30(5), O2–Cu1–N3 94.83(5), N1–Cu1–N2 85.63(5), N1–Cu1–N3 86.28(5), N2–Cu1–N3 151.23(5).

N1 2.241(3) Å, Zn2–N6 2.257(3) Å] are considerably longer than the Zn–N$_{\text{primary}}$ separations [range 2.025(4)–2.052(3) Å]. The Zn–O$_{\text{amide}}$ distances [Zn1–O2 2.053(2) Å, Zn2–O1 2.065(2) Å] are slightly longer than the Zn–O$_{\text{acetato}}$ distances [Zn1–O5 1.997(3) Å, Zn2–O1 2.008(3) Å].

The molecular structures of the copper complexes **6a**·MeOH and **6b**·2DMF also exhibit pentacoordinate metal centers. Both compounds crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$ for **6a**·MeOH and $Z = 1$ for **6b**·2DMF (inversion center at the midpoint of the C7–C7* bond). The methanol molecule and some of the fluoride atoms are disordered in **6a**·MeOH.

In both **6a**·MeOH and **6b**·2DMF, the copper ions adopt a tetragonal-pyramidal coordination geometry (**6a**·MeOH: $\tau = 0.12$ for Cu1 and $\tau = 0.29$ for Cu2; **6b**·2DMF: $\tau = 0.37$) with the amide oxygen atoms residing in the apical positions (Figure 2). The Cu1–O$_{\text{apical}}$ bond lengths [**6a**·MeOH: 2.336(3) Å and 2.218(3) Å; **6b**·2DMF: 2.2585(10) Å] are notably longer than the equatorial bond lengths which exhibit approximately equidistant lengths of about 2.0 Å.

The metal atoms in the dinickel complexes **7a**(MeOH)$_2$·0.5MeOH and **7b**·2MeCN are coordinated in a distorted octahedral fashion (Figure 3). Both tetrafluoroacetate anions per Ni$^{\text{II}}$ are coordinated to the metal centers in **7b**·2MeCN leading to a neutral complex. The metal centers in compound **7a**(MeOH)$_2$·0.5MeOH are coordinated by a tetrafluoroacetate anion and a methanol molecule. The remaining two tetrafluoroacetate anions crystallize as counteranions with partially disordered fluorine atoms. All Ni–N and Ni–O distances fall in a narrow range of 2.095(3)–2.103(3) Å [**7a**(MeOH)$_2$·0.5MeOH] and 2.058(3)–2.113(4) Å (**7b**·2MeCN).

The metal-donor bond lengths and angles for all complexes of types **5**–**7** with the neutral diamide ligands fall in the range reported previously for similar complexes with an unbridged tripodal ligand with amide and pyridyl donor functions.[7] Complexes with ligand H$_2$-**4a** possess amide groups with the NCO units twisted out of the plane of the aromatic spacer, most likely caused by the steric repulsion of the two amide protons. Due to the more flexible ethylene

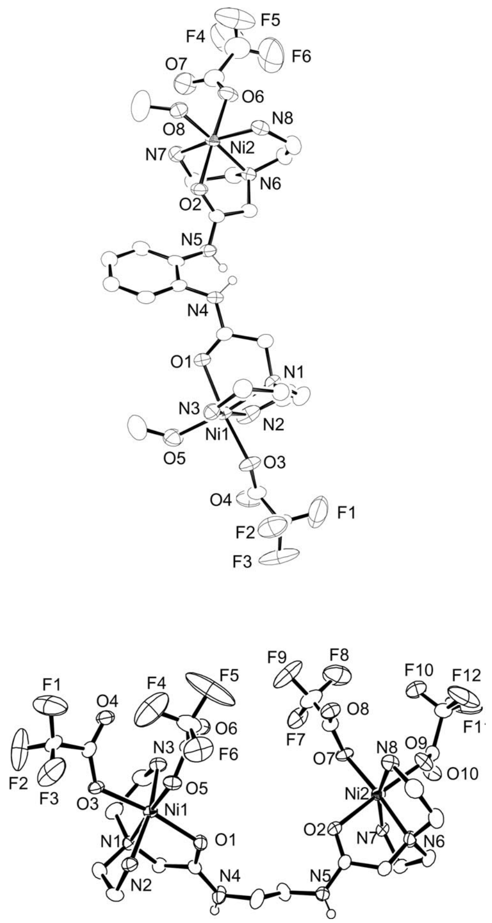
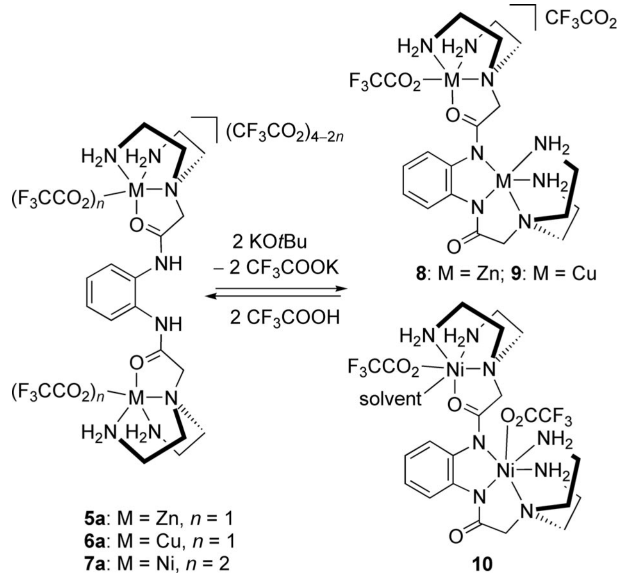


Figure 3. Molecular structures of the complex cations in **7a**(MeOH)$_2$·0.5MeOH (top, uncoordinated counterions and hydrogen atoms except amide N–H protons are omitted for clarity) and of **7b** in **7b**·2MeCN. Selected bond lengths [Å] and angles [°] for **7a**MeOH)$_2$·0.5MeOH: Ni1–O1 2.065(3), Ni1–O3 2.061(3), Ni1–O5 2.073(3), Ni1–N1 2.100(4), Ni1–N2 2.095(4), Ni1–N3 2.088(4), Ni2–O2 2.083(3), Ni2–O6 2.103(3), Ni2–O8 2.059(3), Ni2–N6 2.090(3), Ni2–N7 2.075(4), Ni2–N8 2.087(4); O1–Ni1–O3 172.49(12), O1–Ni1–O5 91.58(13), O1–Ni1–N1 81.86(12), O1–Ni1–N2 92.56(14), O1–Ni1–N3 93.02(13), N1–Ni1–N2 83.8(2), N1–Ni1–N3 83.78(15), N2–Ni1–N3 165.5(2), O2–Ni2–O6 175.76(13), O2–Ni2–O8 91.78(13), O2–Ni2–N6 81.73(12), O2–Ni2–N7 87.91(14), O2–Ni2–N8 97.82(13), N6–Ni2–N7 84.98(14), N6–Ni2–N8 82.64(14), N7–Ni2–N8 165.5(2). Selected bond lengths [Å] and angles [°] for **7b**·2MeCN: Ni1–O1 2.093(3), Ni1–O3 2.090(3), Ni1–O5 2.067(3), Ni1–N1 2.095(4), Ni1–N2 2.106(4), Ni1–N3 2.091(4), Ni2–O2 2.082(3), Ni2–O7 2.058(3), Ni2–O9 2.082(3), Ni2–N6 2.093(4), Ni2–N7 2.113(4), Ni2–N8 2.097(4); O1–Ni1–O3 172.49(11), O1–Ni1–O5 96.90(12), O1–Ni1–N1 81.90(12), O1–Ni1–N2 91.31(13), O1–Ni1–N3 94.58(14), N1–Ni1–N2 83.42(14), N1–Ni1–N3 83.25(14), N2–Ni1–N3 164.51(15), O2–Ni2–O7 93.15(12), O2–Ni2–O9 176.27(13), O2–Ni2–N6 82.22(13), O2–Ni2–N7 90.13(13), O2–Ni2–N8 97.95(14), N6–Ni2–N7 83.91(14), N6–Ni2–N8 82.85(15), N7–Ni2–N8 163.39(15).

spacer, the arrangement of the two metal centers in the complexes derived from the aliphatic ligand **4b**-H$_2$ are mainly determined by crystal packing effects.

Complexes **5a**–**7a** containing the phenylene-bridged diamide ligand are readily deprotonated at the amide functions by potassium *tert*-butoxide in methanol to yield the complexes **8**–**10** (Scheme 3). The deprotonation reaction is accompanied by a rearrangement in the coordination environment of one of the metal centers in the dinuclear complexes. The two amidate nitrogen atoms formed by deprotonation now coordinate to one metal center while the coordination geometry of the second metal center remains unchanged. The switch in the coordination mode is fully reversible upon protonation of the amidate nitrogen atoms with trifluoroacetic acid (Scheme 3). For the copper complex **6a** the rearrangement of the coordination sphere upon deprotonation to give complex **9** is accompanied by a characteristic color change from blue for **6a** to green for **9**.



8: M = Zn; **9**: M = Cu

5a: M = Zn, *n* = 1
6a: M = Cu, *n* = 1
7a: M = Ni, *n* = 2

10

Scheme 3. Reversible deprotonation of complexes **5a**–**7a** accompanied by a structural rearrangement to yield the unsymmetrical complexes **8**–**10**.

Crystals of **8**·3MeOH, **9**·MeOH, and (**10**)$_2$·2MeOH·2Et$_2$O suitable for X-ray diffraction analyses were obtained by slow diffusion of diethyl ether into methanol solutions of the complexes. The dinuclear zinc complex in **8**·3MeOH (Figure 4) features two different pentacoordinate zinc atoms. One of them (Zn2) exhibits a coordination environment which is unchanged compared to the starting complex **5a** with the zinc atom coordinated by three aliphatic amine donors from the tripodal subunit, one amide oxygen atom and one oxygen atom from a trifluoroacetate anion. The second zinc atom (Zn1) is also coordinated by three aliphatic amine donors in addition to two amidate nitrogen atoms with the amide oxygen atom remaining uncoordinated. The coordination geometry of atom Zn1 is also best described as trigonal-bipyramidal (τ = 0.67) with the tertiary amine (N5) and one of the amidate donor functions (N1) in the axial positions. The Zn–N$_{tert}$ bond length is the longest Zn-donor separation for both zinc atoms [Zn1–N5 2.270(3) Å, Zn2–N6 2.253(3) Å]. Although zinc atom Zn1 is slightly displaced from the plane of the aromatic ring, bond lengths and angles involving atoms Zn1, N1 and N2 correspond well to those reported for a mononuclear zinc complex of a bis(tripodal) amine ligand with an *ortho*-phenanthroline spacer.[13]

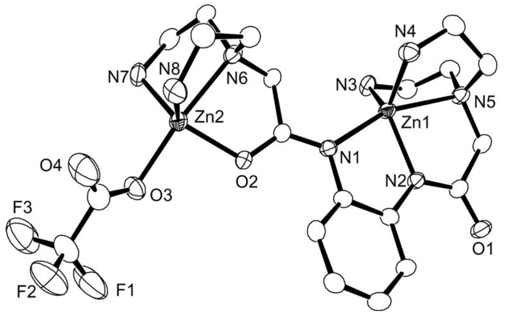


Figure 4. Molecular structure of the complex cation in **8**·3MeOH (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Zn1–N1 2.089(3), Zn1–N2 2.008(3), Zn1–N3 2.063(3), Zn1–N4 2.063(3), Zn1–N5 2.270(3), Zn2–O2 2.027(2), Zn2–O3 2.034(3), Zn2–N6 2.252(3), Zn2–N7 2.066(3), Zn2–N8 2.055(3); N1–Zn1–N5 160.77(11), N2–Zn1–N3 117.44(12), N2–Zn1–N4 120.60(13), N3–Zn1–N4 114.48(13), O3–Zn2–N6 172.11(11), O3–Zn2–N6 172.11(11), O2–Zn2–N7 131.01(12), O2–Zn2–N8 110.13(12), N7–Zn2–N8 109.84(13).

The unsymmetrical copper complex **9**·MeOH (Figure 5) contains a tetragonal-pyramidal copper atom Cu2 exhibiting a coordination environment which is identical and bond parameters which are not significantly different from those observed for the tetragonal-pyramidal copper atoms in complex **6a**·MeOH. Copper atom Cu1 adopts a coordination geometry in between tetragonal-pyramidal and trigonal-bipyramidal (τ-value of 0.58). The Cu1–$N_{amidate}$ bond lengths are the shortest Cu1-donor separations and are in good agreement with the corresponding bond lengths observed for the copper complex with a deprotonated *ortho*-phenylenediamide ligand.[6]

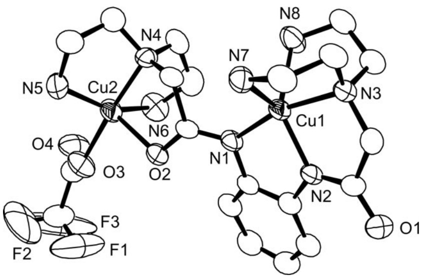


Figure 5. Molecular structure of the complex cation in **9**·MeOH (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu1–N1 1.982(6), Cu1–N2 1.929(6), Cu1–N3 2.045(6), Cu1–N7 2.143(6), Cu1–N8 2.159(7), Cu2–O2 2.196(5), Cu2–O3 1.953(6), Cu2–N4 2.043(6), Cu2–N5 1.993(7), Cu2–N6 2.007(8); N1–Cu1–N3 165.3(2), N2–Cu1–N7 126.7(3), N2–Cu1–N8 130.6(3), N7–Cu1–N8 98.3(3), O2–Cu2–O3 90.3(2), O2–Cu2–N4 81.5(2), O2–Cu2–N5 113.0(3), O2–Cu2–N6 89.7(3), O3–Cu2–N4 170.9(3), O3–Cu2–N5 94.7(3), O3–Cu2–N6 98.3(3), N4–Cu2–N5 85.1(3), N4–Cu2–N6 85.6(3), N5–Cu2–N6 153.8(3).

The nickel complex **10** dimerizes upon crystallization via formation of two intermolecular amide-O–Ni interactions (O1–Ni2 and O1*–Ni2) and formation of the tetranuclear complex $(\mathbf{10})_2$·2MeOH·2Et_2O in the solid state. The tetranuclear complex resides on a crystallographic inversion center (Figure 6).

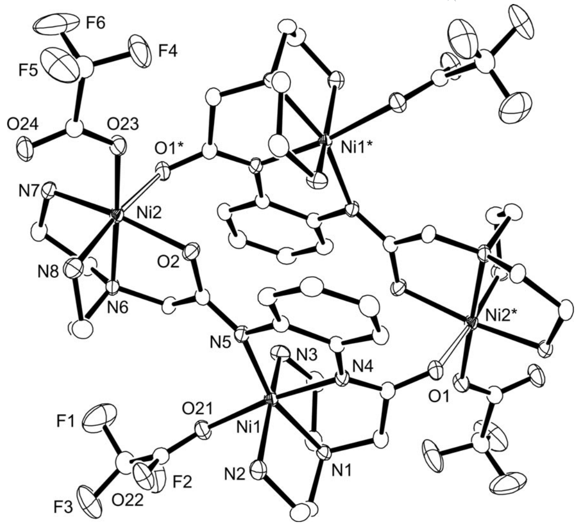
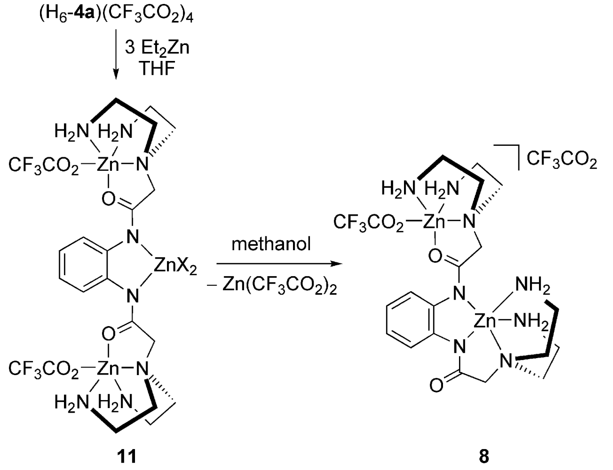


Figure 6. Molecular structure of the tetranuclear nickel complex in $(\mathbf{10})_2$·2MeOH·2Et_2O (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ni1–N1 2.122(2), Ni1–N2 2.106(2), Ni1–N3 2.108(2), Ni1–N4 2.004(2), Ni1–N5 2.094(2), Ni1–O21 2.229(15), Ni2–N6 2.083(2), Ni2–N7 2.081(2), Ni2–N8 2.104(2), Ni2–O1 2.1744(15), Ni2–O2 2.0455(14), Ni2–O23 2.0531(15); N1–Ni1–N5 161.11(7), N2–Ni1–N3 160.05(7), N4–Ni1–O21 171.22(6), N6–Ni2–O23 174.98(7), N7–Ni2–O2 163.64(6), N8–Ni2–O1 174.03(6).

Both of the two different nickel centers in one molecule of **10** exhibit a distorted octahedral coordination geometry. Atom Ni1 is coordinated by the two amidate nitrogen atoms, three amines of one tripodal subunit, and a trifluoroacetate counterion. Atom Ni2 has a coordination environment similar to the nickel atoms in complex **7a**$(MeOH)_2$ with the methanol donor in **7a**$(MeOH)_2$ replaced by an amide oxygen atom from a neighboring molecule of **10**. The most remarkable structural feature of $(\mathbf{10})_2$ is the unusual coordination mode of the doubly deprotonated diamide spacer of the deprotonated ligand $\mathbf{4a}^{2-}$ which coordinates with all four donor atoms of the two amidate groups (N4, N5, O1, O2) to three different metal centers (Ni1, Ni2 and Ni2*). Although such a binding mode is common for 1,2-bis(oxamato)arenes[14] it has not been reported for *ortho*-phenylene-bridged acetamides yet.

Reaction of the trifluoroacetate salt $(H_6\text{-}\mathbf{4a})(CF_3CO_2)_4$ with three equivalents of diethylzinc results in the formation of the trinuclear zinc complex **11** (Scheme 4) via deprotonation of the four primary ammonium groups and of the two amide groups of the aromatic spacer. Both the ^1H and ^{13}C NMR spectra of **11** show only one set of resonances indicative for the formation of a symmetrical complex. Coordination of the two amidate nitrogen atoms of the deprotonated ligand $\mathbf{4a}^{2-}$ to the zinc center leads to a higher degree of coplanarity of the aromatic ring and the amides NCO units compared to the dinuclear complex **5a**. The electron withdrawing effect of the zinc ions coordinated to the amide carbonyl oxygen atoms is mediated by the extended π-system formed this way causing a considerable deshielding of the aromatic protons in the *ortho*-position to the amide substituents (δ = 7.76 ppm for **5a**, δ = 8.85 ppm for **11**).



Scheme 4. Synthesis of the symmetric trinuclear zinc complex **11** and degradation to the unsymmetric dinuclear complex **8** in methanol.

Complex **11** is quickly degraded in methanol to give the unsymmetrical complex **8** (Scheme 4) obtained previously by deprotonation of complex **5a**. The protic solvent facilitates the entropically favored elimination of one equivalent of zinc trifluoroacetate associated with a rearrangement of the complex, as was observed for **5a** upon deprotonation. Crystals of the decomposition product of **11** with the composition $[Zn(CF_3CO_2)($**4a**$)](CF_3CO_2)\cdot[Zn($**4a**$)(MeOH)][Zn(CF_3CO_2)_4]$ were obtained by slow diffusion of diethyl ether into a solution of the compound in methanol. The structure analysis (see Supporting Information) shows that the elimination and rearrangement to the unsymmetrical dinuclear zinc complex did indeed occur. The asymmetric unit contains one formula unit of $[Zn(CF_3CO_2)($**4a**$)]CF_3CO_2$ **8** and another dinuclear zinc complex also with an unsymmetrical coordinated ligand **4a** and a $[Zn(CF_3CO_2)_4]^{2-}$ counterion. The bond parameters of the two complex anions are nearly identical and match those for **8** obtained by deprotonation of complex **5a**.

Conclusions

The neutral diamide ligands H_2-**4a** and H_2-**4b** preferably coordinate to divalent metal ions like Zn^{2+}, Cu^{2+} or Ni^{2+} via the aliphatic amine donors and the carbonyl oxygen atoms of the amide groups. The symmetrical dinuclear complexes **5a**, **6a** and **7a** of the phenylene-bridged ligand H_2-**4a** are readily deprotonated by alcoholates at the amide functions which causes a rearrangement of the coordinated donor groups and coordination of the generated two amidate nitrogen atoms to one of the metal centers. This rearrangement is fully reversible by protonation of the amide functions.

Experimental Section

General: All operations were carried out under an atmosphere of dry argon using Schlenk and vacuum techniques. Solvents were dried by standard methods and freshly distilled prior to use. NMR spectra were recorded at 298 K with Bruker AC 200 (200 MHz) or Bruker AMX 400 (400 MHz) spectrometers and are reported relative to the solvent signal. IR spectra were measured with a Bruker Vector 22 IR spectrometer. Mass spectra were obtained with a Bruker Reflex IV (MALDI) spectrometer. Elemental analyses were performed with a Vario EL III CHNS analyzer. The *N*,*N′*-bis(bromoacetyl)diamines **1a** and **1b**, bis(2-*tert*-butoxycarbonylaminoethyl)amine (**2**), and diamide **3a** were synthesized as described previously.[15,16] Consistent elemental analyses of the ligand precursors $(H_6$-**4a**$)(CF_3CO_2)_4$ and $(H_6$-**4b**$)(CF_3CO_2)_4$ and for the metal complexes were difficult to obtain due to the presence of the trifluoro acetate ions.

Diamide 3b: Diamide **3b** was synthesized as described for diamide **3a**[16] from **1b** (7.55 g, 25 mmol) and bis(2-*tert*-butoxycarbonylaminoethyl)amine (**2**) (15.15 g, 50 mmol); yield 14.99 g (20.1 mmol, 80%) of a colorless solid. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.39 [s, 2 H, N*H*C(O)CH_2], 6.11 (s, 4 H, NHBoc), 3.33 [s, 4 H, NHC(O)C*H_2*N], 2.96 (t, 8 H, NCH_2C*H_2*NHBoc), 2.80 [s, 4 H, C*H_2*NHC(O)CH_2N], 2.28 (t, 8 H, NC*H_2*CH_2NHBoc), 1.25 [s, 36 H, C(O)OC$(CH_3)_3$] ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 171.0 [NH*C*(O)CH_2], 156.7 [*C*(O)O*t*Bu], 79.1 [C(O)O*C*$(CH_3)_3$], 58.4 [NHC(O)*C*H_2N], 55.0 (NCH_2*C*H_2NHBoc), 39.0 [*C*H_2NHC(O)CH_2N], 38.3 (N*C*H_2CH_2NHBoc), 28.5 [C(O)OC(*C*$H_3)_3$] ppm. MALDI-MS (TOF, positive ions): *m*/*z* = 785 $[M + K]^+$, 769 $[M + Na]^+$, 747 $[M + H]^+$. $C_{34}H_{66}N_8O_{10}$ (746.95): calcd. C 54.67, H 8.91, N 26.25; found C 54.70, H 8.89, N 26.29.

Trifluoroacetate Salts $(H_6$-4a$)(CF_3CO_2)_4$ and $(H_6$-4b$)(CF_3CO_2)_4$: For the preparation of $(H_6$-**4a**$)(CF_3CO_2)_4$ diamide **3a** (1.34 g, 1.7 mmol) was dissolved in chloroform (50 mL) and trifluoroacetic acid (3.8 mL, 51 mmol) was added. After stirring at ambient temperature for 12 h the solvent was removed under reduced pressure. The oily solid obtained was dissolved in acetonitrile and precipitated by addition of chloroform. The colorless precipitate was collected by filtration and was dried in vacuo. Salt $(H_6$-**4b**$)(CF_3CO_2)_4$ was synthesized in the same way starting from diamide **3b** (1.61 g, 2.2 mmol) and trifluoroacetic acid (4.9 mL, 66 mmol).

$(H_6$-4a$)(CF_3CO_2)_4$: Yield 1.02 g (1.2 mmol, 71%) of a colorless solid. ^{1}H NMR (200.1 MHz, CD_3OD): δ = 7.60 (m, 2 H, Ar-CH), 7.24 (m, 2 H, Ar-CH), 3.59 [s, 4 H, NHC(O)C*H_2*N], 3.10 (t, 8 H, NC*H_2*$CH_2NH_3^+$), 2.95 (t, 8 H, NCH_2C*H_2*NH_3^+) ppm. ^{13}C NMR (50.3 MHz, CD_3OD): δ = 173.6 [NHC(O)], 132.2 (Ar-C_{ipso}), 128.0, 127.6 (Ar-C), 58.5 [NHC(O)*C*H_2N], 54.8 (N*C*$H_2CH_2NH_3^+$), 39.5 (NCH_2*C*$H_2NH_3^+$) ppm. ^{19}F NMR (188.3 MHz, CD_3OD): δ = –72.5 ($CF_3CO_2^-$) ppm. MALDI-MS (TOF, positive ions): *m*/*z* = 417 $[(H_2$-**4a**$)+Na]^+$; 395 $[(H_2$-**4a**$)+H]^+$. IR (KBr): $\tilde{\nu}$ = 3424 (m), 3282 (w), 3059 (w), 2950 (w), 2928 (w), 1686 (s, CO), 1528 (m, CO) cm^{-1}. Crystals of $(H_6$-**4a**$)(CF_3CO_2)_4\cdot 2MeOH$ were obtained by diffusion of diethyl ether into a methanol solution of the compound. For an X-ray diffraction analysis of $(H_6$-**4a**$)(CF_3CO_2)_4\cdot 2MeOH$ see Supporting Information.

$(H_6$-4b$)(CF_3CO_2)_4$: Yield 1.41 g (1.8 mmol, 82%) of a colorless solid. ^{1}H NMR (400.1 MHz, CD_3CN): δ = 8.10 [s, 2 H, NHC(O)], 7.72 (s, 12 H, NCH_2CH_2N*H_3^+*), 3.29 [d, 4 H, C*H_2*NHC(O)], 3.20 [s, NHC(O)C*H_2*N], 3.04 (t, 8 H, NC*H_2*$CH_2NH_3^+$), 2.77 (t, 8 H, NCH_2C*H_2*NH_3^+) ppm. ^{13}C NMR (100.6 MHz, CD_3CN): δ = 174.0 [NHC(O)], 162.2 (q, $^2J_{CF}$ = 34 Hz, CF_3*C*O_2^-), 118.0 (q, $^1J_{CF}$ = 294 Hz, *C*$F_3CO_2^-$), 57.9 [NHC(O)*C*H_2N], 53.4 (N*C*$H_2CH_2NH_3^+$), 40.1 [*C*H_2NHC(O)], 38.5 (NCH_2*C*$H_2NH_3^+$) ppm. MALDI-MS (TOF, positive ions): *m*/*z* = 369 $[(H_2$-**4b**$)+Na]^+$, 347 $[(H_2$-**4b**$)+H]^+$. IR (KBr): $\tilde{\nu}$ = 3343 (m), 3066 (m), 2958 (w), 2855 (w), 2718 (w), 2661 (w), 2618 (w), 2530 (w), 1676 (s, CO), 1558 (m, CO) cm^{-1}.

General Procedure for the Synthesis of the Dinuclear Complexes 5–7 Bearing the Neutral Diamide Ligands (H_2-4a) and (H_2-4b): The metal precursor (0.4 mmol) was dissolved in methanol (5 mL) and a solution of the ligand salt (0.2 mmol) in methanol (5 mL) was added. The reaction mixture was stirred for 12 h at ambient temperature. Subsequently, the solvent was removed under reduced pressure. The residue was dissolved in acetonitrile (5 mL) and diethyl ether (40 mL) was added. In all cases the complexes precipitated and the precipitates were collected by filtration and were dried in vacuo. Except when noted, crystals of the complexes suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into a concentrated solution of the complex in methanol.

[$Zn_2(CF_3CO_2)_2$(H_2-4a)](O_2CCF_3)$_2$ (5a): The complex was synthesized from $Zn(acac)_2{\cdot}H_2O$ (113 mg, 0.4 mmol) and (H_6-**4a**)(CF_3CO_2)$_4$ (170 mg, 0.2 mmol); yield 168 mg (0.17 mmol, 85%) of a colorless solid. ^{1}H NMR (400.0 MHz, CD_3OD): δ = 7.76 (m, 2 H, Ar-H$_{ortho}$), 7.37 (m, 2 H, Ar-H$_{para}$), 3.97 [s, 4 H, NHC(O)-CH_2N], 2.95 (m, 16 H, NCH_2CH$_2$NH$_2$ and NCH$_2$CH_2NH$_2$) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 175.9 [NHC(O)], 163.3 (q, $^2J_{CF}$ = 34.4 Hz, $CF_3CO_2^-$), 130.4 (Ar-C$_{ipso}$), 128.5, 127.2 (Ar-C), 118.1 (q, $^1J_{CF}$ = 294 Hz, $CF_3CO_2^-$), 58.3 [NHC(O)CH_2N], 55.7 (N$CH_2CH_2NH_2$), 38.5 ($NCH_2CH_2NH_2$) ppm. MALDI-MS (TOF, positive ions): m/z = 635 [$Zn_2(CF_3CO_2)$(H_2-**4a**)]–2H$^+$. IR (KBr): $\tilde{\nu}$ = 3315 (m), 3022 (w), 2970 (w), 2926 (w), 2882 (w), 1691 (s, CO), 1641 (s, CO) cm^{-1}.

[$Zn_2(CF_3CO_2)_2$(H_2-4b)](CF_3CO_2)$_2$ (5b): The complex was synthesized from $Zn(CH_3CO_2)_2{\cdot}2H_2O$ (88 mg, 0.4 mmol) and (H_6-**4b**)(CF_3CO_2)$_4$ (160 mg, 0.2 mmol); yield 85 mg (0.09 mmol, 45%) of a colorless solid. ^{1}H NMR (400.1 MHz, CD_3CN): δ = 9.99 [s, 2 H, NHC(O)], 3.55 [s, 4 H, CH_2NHC(O)], 3.51 [m, 4 H, NHC(O)-CH_2N], 3.35 (m, 8 H, NCH$_2$CH$_2$NH_2), 2.78 (m, 16 H, NCH_2CH$_2$NH$_2$ and NCH$_2$CH_2NH$_2$) ppm. ^{13}C NMR (100.6 MHz, CD_3CN): δ = 175.9 [NHC(O)], 161.8 (q, $^2J_{CF}$ = 34.0 Hz, $CF_3CO_2^-$), 118.0 (q, $^1J_{CF}$ = 294 Hz, $CF_3CO_2^-$), 56.9 [NHC(O)-CH_2N], 54.8 (N$CH_2CH_2NH_2$), 40.4 [CH_2NHC(O)], 38.1 ($NCH_2CH_2NH_2$) ppm. MALDI-MS (TOF, positive ions): m/z = 587 {[$Zn_2(CF_3CO_2)$(H_2-**4b**)]–2H}$^+$. IR (KBr): $\tilde{\nu}$ = 3443 (m), 3258 (w), 2961 (w), 2928 (w), 1691 (s, CO), 1629 (s, CO) cm^{-1}.

[$Cu_2(CF_3CO_2)_2$(H_2-4a)](CF_3CO_2)$_2$ (6a): The complex was synthesized from $Cu(acac)_2{\cdot}H_2O$ (112 mg, 0.4 mmol) and (H_6-**4a**)(CF_3CO_2)$_4$ (170 mg, 0.2 mmol); yield 175 mg (0.18 mmol, 90%) of a blue solid. MALDI-MS (TOF, positive ions): m/z = 631 {[$Cu_2(CF_3CO_2)$(H_2-**4a**)]–2H}$^+$. UV/Vis (methanol): λ = 685 nm. IR (KBr): $\tilde{\nu}$ = 3228 (m), 2969 (w), 2894 (w), 2819 (w), 1676 (s, CO), 1545 (m, CO) cm^{-1}.

[$Cu_2(CF_3CO_2)_2$(H_2-4b)](CF_3CO_2)$_2$ (6b): The complex was synthesized from $Cu(acac)_2{\cdot}H_2O$ (112 mg, 0.4 mmol) and (H_6-**4b**)(CF_3CO_2)$_4$ (160 mg, 0.2 mmol); yield 152 mg (0.16 mmol, 80%) of a blue solid. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a solution of the complex in DMF. MALDI-MS (TOF, positive ions): m/z = 583 {[$Cu_2(CF_3CO_2)$(H_2-**4b**)]–2H}$^+$. UV/Vis (methanol): λ = 670 nm. IR (KBr): $\tilde{\nu}$ = 3299 (m), 3239 (m), 3172 (m), 3089 (w), 2965 (w), 2894 (w), 1679 (s, CO), 1639 (s, CO) cm^{-1}.

[$Ni_2(CF_3CO_2)_4$(H_2-4a)] (7a): The complex was synthesized from $Ni(CH_3CO_2)_2{\cdot}4H_2O$ (100 mg, 0.4 mmol) and (H_6-**4a**)(CF_3CO_2)$_4$ (170 mg, 0.2 mmol); yield 167 mg (0.17 mmol, 85%) of a blue solid. MALDI-MS (TOF, positive ions): m/z = 621 {[$Ni_2(CF_3CO_2)$(H_4-**4a**)]–2H}$^+$. UV/Vis (methanol): λ = 979, 588, 372 nm. IR (KBr): $\tilde{\nu}$ = 3367 (m), 3305 (m), 2968 (w), 1683 (s, CO), 1647 (s, CO) cm^{-1}.

[$Ni_2(CF_3CO_2)_4$(H_2-4b)] (7b): The complex was synthesized from $Ni(CH_3CO_2)_2{\cdot}4H_2O$ (100 mg, 0.4 mmol) and (H_6-**4b**)(CF_3CO_2)$_4$ (160 mg, 0.2 mmol); yield 115 mg (0.13 mmol, 65%) of a blue solid. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a solution of the complex in acetonitrile. MALDI-MS (TOF, positive ions): m/z = 573 {[$Ni_2(CF_3CO_2)$(H_2-**4b**)]–2H}$^+$. UV/Vis (methanol): λ = 982, 587, 340 nm. IR (KBr): $\tilde{\nu}$ = 3106 (w), 2957 (w), 1684 (s, CO), 1645 (s, CO) cm^{-1}.

General Procedure for the Deprotonation of Complexes 5a–7a with Formation of Complexes 8, 9 and 10: A sample of one of the dinuclear complexes **5a**–**7a** bearing the neutral diamide ligand (0.2 mmol) was suspended in acetonitrile (20 mL). To this suspension was added 0.1 M solution of KO*t*Bu in methanol (4.0 mL, 0.4 mmol). The resulting solution was stirred for 1 h at ambient temperature. Subsequently, diethyl ether (40 mL) was added. Complexes **8**–**10** precipitated and were collected by filtration and dried in vacuo. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a solution of the complex in methanol.

[$Zn_2(CF_3CO_2)$(4a)](CF_3CO_2) (8): Complex **8** was prepared from complex **5a** (195 mg, 0.2 mmol); yield 123 mg (0.16 mmol, 80%) of a colorless solid. ^{1}H NMR (400.0 MHz, CD_3OD): δ = 8.75 (m, 1 H, Ar-H$_{ortho}$), 8.63 (m, 1 H, Ar-H$_{ortho}$), 6.93 (m, 1 H, Ar-H$_{para}$), 6.86 (m, 1 H, Ar-H$_{para}$), 3.50 {s, 2 H, [C(O)CH_2N]}, 3.31 {s, 2 H, [C(O)CH_2N]}, 2.84 (m, 16 H, NCH_2CH$_2$NH$_2$ and NCH$_2$CH_2NH$_2$) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 172.9, 172.5 [NHC(O)], 163.1 (q, $^2J_{CF}$ = 35.7 Hz, $CF_3CO_2^-$), 140.6, 139.5 (Ar-C$_{ipso}$), 124.3, 124.0, 122.6, 122.0 (Ar-C), 118.3 (q, $^1J_{CF}$ = 292 Hz, $CF_3CO_2^-$), 62.2, 61.4 [C(O)CH_2N], 55.2, 54.5 (N$CH_2CH_2NH_2$), 39.4, 38.3 ($NCH_2CH_2NH_2$) ppm. MALDI-MS (TOF, positive ions): m/z = 635 [$Zn_2(CF_3CO_2)$(**4a**)]$^+$. IR (KBr): $\tilde{\nu}$ = 3316 (m), 3156 (w), 2949 (w), 1685 (s, CO), 1593 (m, CO), 1549 (s, CO) cm^{-1}.

[$Cu_2(CF_3CO_2)$(4a)](CF_3CO_2) (9): Complex **9** was prepared from complex **6a** (195 mg, 0.2 mmol); yield 117 mg (0.16 mmol, 80%) of a dark green solid. MALDI-MS (TOF, positive ions): m/z = 631 [$Cu_2(CF_3CO_2)$(**4a**)]$^+$. UV/Vis (methanol): λ = 766, 670, 439 (sh) nm. IR (KBr): $\tilde{\nu}$ = 3266 (m), 3161 (w), 2947 (w), 2889 (w), 1690 (s, CO), 1594 (m, CO), 1544 (s, CO) cm^{-1}.

[$Ni_2(CF_3CO_2)_2$(4a)] (10): Complex **10** was prepared from complex **7a** (193 mg, 0.2 mmol); yield 97 mg (0.13 mmol, 65%) of a blue solid. MALDI MS (TOF, positive ions): m/z = 621 [$Ni_2(CF_3CO_2)$(**4a**)]$^+$. UV/Vis (methanol): λ = 949, 583, 382 nm. IR (KBr): $\tilde{\nu}$ = 3376 (m), 3316 (m), 2933 (w), 2894 (w), 2864 (w), 1689 (s, CO), 1591 (m, CO), 1543 (s, CO) cm^{-1}.

[($Zn_2(CF_3CO_2)_2$(4a))$Zn(CF_3CO_2)_2$] (11): Salt (H_6-**4a**)(CF_3CO_2)$_4$ (850 mg, 1.0 mmol) was suspended in THF (30 mL) and 3.0 mL of a 1 M solution of diethylzinc in hexane (3.0 mmol) were added dropwise. The resulting solution was stirred for 12 h at ambient temperature. Subsequently, diethyl ether (50 mL) was added. A colorless solid precipitated which was collected by filtration and dried in vacuo; yield 943 mg (0.91 mmol, 91%) of a colorless solid. ^{1}H NMR (400.1 MHz, CD_3CN): δ = 8.55 (m, 2 H, Ar-H$_{ortho}$), 6.97 (m, 2 H, Ar-H$_{para}$), 3.72 {s, 4 H, [C(O)CH_2N]}, 3.09 (s, 8 H, NCH$_2$CH$_2$NH_2), 2.78 (m, 16 H, NCH_2CH$_2$NH$_2$ and NCH$_2$CH_2NH$_2$) ppm. ^{13}C NMR (100.6 MHz, CD_3CN): δ = 174.0 [NHC(O)], 161.9 (q, $^2J_{CF}$ = 35.7 Hz, $CF_3CO_2^-$), 139.1 (Ar-C$_{ipso}$), 123.9, 123.8 (Ar-C), 117.7 (q, $^1J_{CF}$ = 291 Hz, $CF_3CO_2^-$), 61.0 [C(O)CH_2N], 54.6 (N$CH_2CH_2NH_2$), 38.1 ($NCH_2CH_2NH_2$) ppm. MALDI-MS (TOF, positive ions): m/z = 635 [$Zn_2(CF_3CO_2)$(**4a**)]$^+$. Only a dinuclear complex, which is apparently identical to **8** was detected by mass spectrometry. The instability of **11** towards decomposition to **8** was also observed when complex **11** was dissolved in methanol. Dissolving of the trinuclear complex **11** (520 mg, 0.5 mmol) in methanol (10 mL) followed by addition of diethyl ether (50 mL) leads to precipitation of **8** together with zinc trifluoroacetate as a non separable impurity. Crystals of $[Zn(CF_3CO_2)$-(**4a**)](CF_3CO_2)·[Zn(**4a**)(MeOH)]-$[Zn(CF_3CO_2)_4]$ which were suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a solution of the unpurified reaction product in methanol. For an X-ray diffraction study of $[Zn(CF_3CO_2)$-(**4a**)](CF_3CO_2)·[Zn(**4a**)(MeOH)]$[Zn(CF_3CO_2)_4]$ see Supporting Information.

X-ray Diffraction Studies: Diffraction data were collected at T = 153(2) K with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) for **5a**·MeOH, **6a**·MeOH, **6b**·2DMF, (**7a**)$(MeOH)_2$·0.5MeOH, **7b**·2MeCN and $(\mathbf{10})_2$·2MeOH·$2Et_2O$ and with a Bruker AXS SMART CCD diffractometer equipped with a rotation anode using Goebel-mirror monochromated Cu-K_α radiation (λ = 1.54178 Å) for **8**·3MeOH and **9**·MeOH. Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[17] program package. Structures were solved with the SHELXTL-97[18] package using the heavy-atom method and were refined with SHELXL-97[19] against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models in calculated positions.

CCDC-764055 (for **5a**·MeOH), -746056 (for **6a**·MeOH), -746057 (for **6b**·2DMF), -746058 (for **7a**$(2MeOH)_2$·0.5MeOH), -746059 (for **7b**·2MeCN), -746060 (for **8**·3MeOH), -746062 (for **9**·MeOH) and -746057 (for $(\mathbf{10})_2$·2MeOH·$2Et_2O$) contain the supplemantary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for $[Zn_2(CF_3CO_2)_2(H_2\text{-}4a)](CF_3CO_2)_2$·MeOH (5a·MeOH): $C_{27}H_{38}N_8F_{12}O_{11}Zn_2$, M = 1009.42, triclinic, $P\bar{1}$, Z = 2, a = 10.518(3), b = 12.369(3), c = 15.020(4) Å, α = 94.227(6), β = 90.735(5), γ = 99.474(5)°, V = 1921.5(8) Å^3, 19093 measured reflections, 8819 unique reflections (R_{int} = 0.0546), R = 0.0534, wR = 0.1062 for 5827 contributing reflections $[I \geq 2\sigma(I)]$.

Crystal Data for $[Cu_2(CF_3CO_2)_2(H_2\text{-}4a)](CF_3CO_2)_2$·MeOH (6a·MeOH): $C_{27}H_{38}N_8Cu_2F_{12}O_{11}$, M = 1005.73, triclinic, $P\bar{1}$, Z = 2, a = 10.1222(3), b = 11.1517(4), c = 18.9396(6) Å, α = 80.7870(10), β = 77.1800(10), γ = 87.1450(10)°, V = 2057.49(12) Å^3, 25602 measured reflections, 12927 unique reflections (R_{int} = 0.0197), R = 0.0848, wR = 0.2577 for 10091 contributing reflections $[I \geq 2\sigma(I)]$.

Crystal Data for $[Cu_2(CF_3CO_2)_2(H_2\text{-}4b)](CF_3CO_2)_2$·2DMF (6b·2DMF): $C_{28}H_{48}N_{10}Cu_2F_{12}O_{12}$, M = 1071.84, triclinic, $P\bar{1}$, Z = 1, a = 9.8653(8), b = 10.1077(8), c = 11.5686(9) Å, α = 82.1400(10), β = 80.2760(10), γ = 69.9340(10)°, V = 1064.10(15) Å^3, 12904 measured reflections, 6611 unique reflections (R_{int} = 0.0166), R = 0.0327, wR = 0.0883 for 5872 contributing reflections $[I \geq 2\sigma(I)]$.

Crystal Data for $[Ni_2(CF_3CO_2)_2(H_2\text{-}4a)(MeOH)_2](CF_3CO_2)_2$·0.5MeOH (7a$(MeOH)_2$·0.5MeOH): $C_{28.5}H_{44}N_8F_{12}Ni_2O_{12.5}$, M = 1044.14, triclinic, $P\bar{1}$, Z = 2, a = 12.3714(7), b = 12.4745(7), c = 15.4866(9) Å, α = 69.6920(10), β = 71.2890(10), γ = 76.0320(10)°, V = 2100.1(2) Å^3, 20004 measured reflections, 9039 unique reflections (R_{int} = 0.0391), R = 0.0634, wR = 0.1719 for 6546 contributing reflections $[I \geq 2\sigma(I)]$.

Crystal Data for $[Ni_2(CF_3CO_2)_4(H_2\text{-}4b)]$·2MeCN (7b·2MeCN): $C_{26}H_{40}N_{10}F_{12}Ni_2O_{10}$, M = 998.02, monoclinic, $P2_1/c$, Z = 4, a = 15.7631(5), b = 14.8340(5), c = 16.7906(5) Å, β = 91.8110(10)°, V = 3924.2(2) Å^3, 34074 measured reflections, 7633 unique reflections (R_{int} = 0.0494), R = 0.0563, wR = 0.1444 for 5687 contributing reflections $[I \geq 2\sigma(I)]$.

Crystal Data for $[Zn_2(CF_3CO_2)(4a)](CF_3CO_2)$·3MeOH (8·3MeOH): $C_{25}H_{44}N_8F_6O_9Zn_2$, M = 845.46, monoclinic, $P2_1/n$, Z = 4, a = 11.1232(11), b = 11.1663(8), c = 29.677(2) Å, β = 100.377(6)°, V = 3625.8(5) Å^3, 20991 measured reflections, 6425 unique reflections (R_{int} = 0.0588), R = 0.0498, wR = 0.1247 for 4700 contributing reflections $[I \geq 2\sigma(I)]$.

Crystal Data for $[Cu_2(CF_3CO_2)(4a)](CF_3CO_2)$·MeOH (9·MeOH): $C_{23}H_{36}N_8Cu_2F_6O_7$, M = 777.69, triclinic, $P\bar{1}$, Z = 2, a = 11.3617(7), b = 11.6130(6), c = 13.2967(9) Å, α = 110.445(4), β = 103.036(4), γ = 96.414(4)°, V = 1566.3(2) Å^3, 9081 measured reflections, 5261 unique reflections (R_{int} = 0.0550), R = 0.0888, wR = 0.2372 for 3663 contributing reflections $[I \geq 2\sigma(I)]$.

Crystal Data for $[(Ni_2(CF_3CO_2)_2(4a))_2]$·2MeOH·$2Et_2O$ $[(10)_2$·2MeOH·$2Et_2O]$: $C_{54}H_{92}N_{16}F_{12}Ni_4O_{16}$, M = 1684.28, monoclinic, $P2_1/n$, Z = 2, a = 14.3330(4), b = 15.7163(4), c = 15.8825(4) Å, β = 96.3460(10)°, V = 3555.8(2) Å^3, 41385 measured reflections, 10353 unique reflections (R_{int} = 0.0496), R = 0.0397, wR = 0.0896 for 7679 contributing reflections $[I \geq 2\sigma(I)]$.

Supporting Information (see also the footnote on the first page of this article): Structure data of $(H_6\text{-}\mathbf{4a})(CF_3CO_2)_2$·2MeOH and $[Zn(CF_3CO_2)(\mathbf{4a})](CF_3CO_2)$·[Zn(**4a**)(MeOH)]$[Zn(CF_3CO_2)_4]$.

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