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Halido-Bridged Dinuclear Nickel and Zinc Complexes with a Bis(tripodal) Octaamine Ligand – Unusual Coordination Mode of an *ortho*-Phenylenediamine

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A potentially dinucleating octaamine ligand H_6-**4** consisting of two aliphatic tripodal tetraamine units connected by an *ortho*-phenylenediamine spacer has been synthesized. Treatment of H_6-**4** with $Ni(BF_4)_2{\cdot}6H_2O$ or H_{10}-**4**$(BF_4)_4$ with Et_2Zn in the presence of a halide source leads to the formation of the dinuclear complexes $[Ni_2(\mu\text{-}Cl)_2(H_6\text{-}\mathbf{4})](BF_4)_2$ (**5**) and $[Zn(\mu\text{-}F)(H_6\text{-}\mathbf{4})](BF_4)_3$ (**6**), respectively, which were structurally characterized by X-ray diffraction studies. In both **5** and **6** the ligand coordinates with four nitrogen donors to each metal center. The *ortho*-phenylenediamine bridging unit coordinates in an unprecedented fashion with each of its amine functions to only one of the metal centers. The dinickel complex **5** possesses two bridging chlorido ligands that differ notably in their Cl–Ni bond lengths, due to interactions of four amine N–H protons with one of the chlorido bridges leading to a reduced donor ability. The dizinc complex **6** was synthesized without addition of an external halide source. The two zinc atoms in **6** facilitate the abstraction of a fluoride from a tetrafluoroborate anion through a cooperative activation by the two adjacent metal centers.

Introduction

In many naturally occurring enzymes the metal ions are coordinated mainly or even exclusively by nitrogen donor groups.[1,2] Dinuclear metal complexes have received substantial scientific interest as model systems for various metalloenzymes. The dinuclear nickel(II)[3] and zinc(II)[4] complexes of several dinucleating ligands consisting of two connected tripodal or macrocyclic entities with aromatic and aliphatic nitrogen donor functions have been studied by Meyer et al. All of these ligands contain a pyrazole-based bridging unit, which coordinates in its deprotonated form with each nitrogen donor to only one metal center resulting in the proximity of the metal atoms essential for cooperative effects.[4b] Contrary to this situation, *ortho*-phenanthrolines exclusively coordinate as chelating ligands with both nitrogen atoms to the same metal center. Hence, dinucleating ligands based on this bridging group coordinate to metal ions either without participitation of the spacer[5] or in an unsymmetric mode, leading to long distances between the metal centers.[6] *ortho*-Phenylenediamines – in the neutral as well as in the deprotonated form – usually coordinate in a fashion similar to *ortho*-phenanthrolines. Nevertheless, examples for different coordination modes are known such as the coordination of a deprotonated *ortho*-phenylenediamine as a bidentate chelate ligand to one metal atom with concomitant bridging coordination of one of the deprotonated aminato donor groups to another metal center.[7,8] The coordination of an *ortho*-phenylenediamine with its amine functions acting as monodentate donors to two discrete metal centers should be possible as well, but has not been reported yet, probably due to the strong chelating effect of the ligand. Some exceptions have been observed in related macrocyclic ligands.[9]

Here we describe the synthesis of a new bis(tripodal) amine ligand with an *ortho*-phenylenediamine bridging unit and its dinuclear nickel(II) and zinc(II) complexes. These complexes are the first structurally characterized examples of an *ortho*-phenylenediamine ligand coordinating with its amine donor functions to two individual metal centers.

Results and Discussion

The octaamine ligand H_6-**4** was synthesized as shown in Scheme 1. First *ortho*-phenylenediamine was treated with bromoacetyl bromide in the presence of triethylamine as base to afford the dibromide **1**. Substitution of the bromides under basic conditions by amine **2** bearing the *tert*-butoxycarbonyl (Boc) protecting groups gave the Boc-protected diamide **3**. The final step of the ligand synthesis was the reduction of **3** with lithium aluminum hydride in boiling thf under concurrent transformation of the *N*-Boc substituents to methyl groups.

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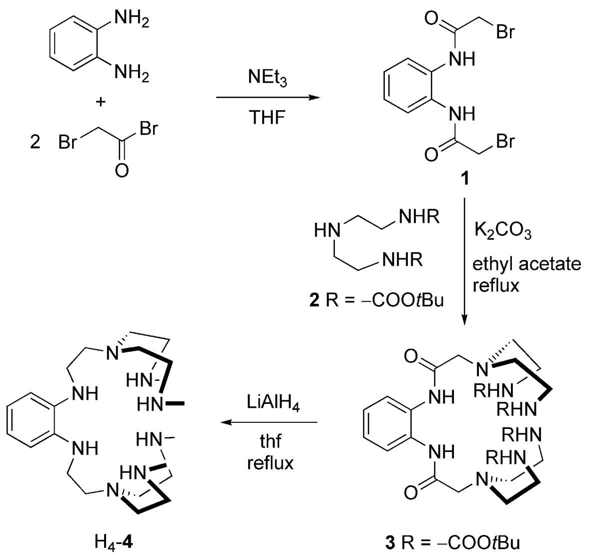
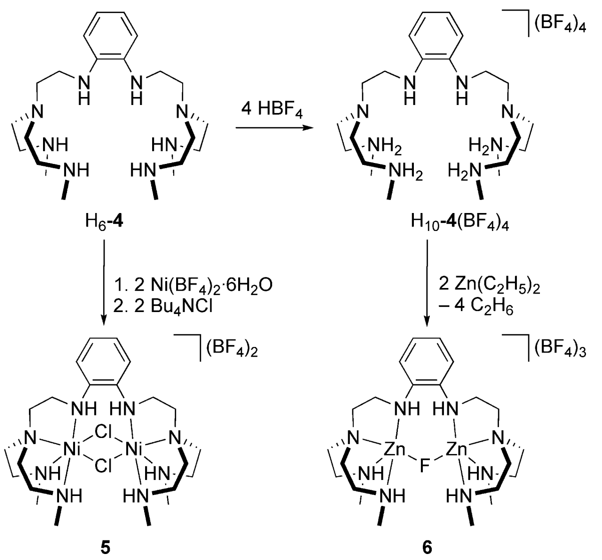


Scheme 1. Synthesis of the bis(tripodal) octaamine ligand H_6-**4**.



Scheme 2. Synthesis of the dinuclear complexes **5** and **6**.

The dinuclear nickel complex $[Ni_2(\mu\text{-}Cl)_2(H_6\text{-}\mathbf{4})](BF_4)_2$ (**5**) was obtained by the reaction of nickel tetrafluoroborate hexahydrate with ligand H_6-**4** in thf followed by the addition of tetrabutylammonium chloride dissolved in acetonitrile (Scheme 2). Addition of diethyl ether to the resulting dark green solution led to precipitation of complex **5** as a green solid. For the synthesis of the dizinc complex $[Zn_2(\mu\text{-}F)_2(H_6\text{-}\mathbf{4})](BF_4)_3$ (**6**) ligand H_6-**4** was first protonated with 4 equiv. of trifluoroboronic acid in thf and precipitated as $(H_{10}\text{-}\mathbf{4})(BF_4)_4$. The thf suspension was subsequently treated with diethylzinc with formation of 4 equiv. of ethane and complex **6** bearing ligand H_6-**4**. Addition of acetonitrile to the reaction mixture gave a colorless solution from which complex **6** was precipitated by addition of diethyl ether. In the case of the dizinc complex, the addition of an external halide source was not necessary. The bridging fluorido ligand in **6** originates from one of the tetrafluoroborate counterions. Fluoride abstraction from tetrafluoroborate anions in the presence of Lewis-acidic metal centers is well known,[10a] and the cooperative activation by two metal centers in close proximity facilitates the abstraction under mild conditions.[10b]

The paramagnetic complex **5** was characterized by IR and UV/Vis spectroscopy, the latter method (methanol solution) showing the typical absorptions for an octahedral *cis*-$\{Ni(Cl)_2(N)_4\}$ chromophore at λ = 376, 605 and 996 nm.[11] The ESI mass spectrum exhibits a peak at m/z = 305.1 for the $[Ni_2(Cl)_2(H_6\text{-}\mathbf{4})]^{2+}$ cation. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded for **6**. Cations $[Zn_2F(H_6\text{-}\mathbf{4})]^{3+}$ (m/z = 190.4) and $[Zn_2F(H_6\text{-}\mathbf{4}) - H]^{2+}$ (m/z = 285.1) were identified in the ESI mass spectrum of **6**.

Green crystals of **5** and colorless crystals of **6**·CH_3CN were obtained by diffusion of diethyl ether into methanol or acetonitrile solutions, respectively, of the complexes **5** and **6** at ambient temperature. Both nickel centers in the dication of **5** (Figure 1) are coordinated in a distorted octahedral fashion, each by the four amine functions of one tripodal unit and two chlorido ligands, which in turn coordinate in a bridging mode to both of the metal centers. The nickel atoms are coordinated by three different types of amine donors of a tripodal tetraamine. A similar situation has been found in complexes of unsymmetrical tripodal tetraamines with different lengths of the spacers between the central nitrogen atom and the primary amine donor functions.[12]

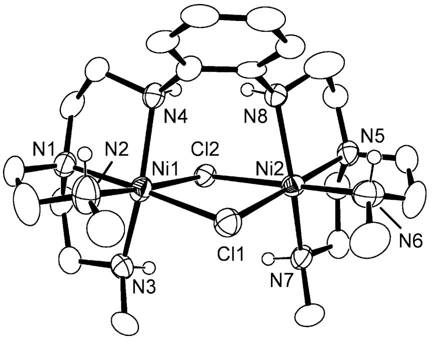


Figure 1. Molecular structure of the complex dication in **5** (C–H protons have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Ni1–Cl1 2.358(2), Ni1–Cl2 2.5769(15), Ni1–N1 2.095(4), Ni1–N2 2.085(5), Ni1–N3 2.108(4), Ni1–N4 2.187(4), Ni2–Cl1 2.334(2), Ni2–Cl2 2.6069(14), Ni2–N5 2.086(5), Ni2–N6 2.080(5), Ni2–N7 2.115(4), Ni2–N8 2.172(4), N3···Cl2 3.165, N4···Cl2 3.097, N7···Cl2 3.117, N8···Cl2 3.127; Cl1–Ni1–Cl2 84.28(5), Cl1–Ni1–N1 176.29(13), Cl1–Ni1–N2 93.85(15), Cl1–Ni1–N3 95.94(13), Cl1–Ni1–N4 99.82(12), Cl2–Ni1–N1 99.09(13), Cl2–Ni1–N2 174.5(2), Cl2–Ni1–N3 84.36(12), Cl2–Ni1–N4 80.64(12), N1–Ni1–N2 82.9(2), N1–Ni1–N3 82.9(2), N1–Ni1–N4 82.3(2), N2–Ni1–N3 100.9(2), N2–Ni1–N4 94.7(2), N3–Ni1–N4 157.0(2), Cl1–Ni2–Cl2 84.09(5), Cl1–Ni2–N5 177.04(13), Cl1–Ni2–N6 94.54(15), Cl1–Ni2–N7 98.80(13), Cl1–Ni2–N8 96.89(12), Cl2–Ni2–N5 98.17(13), Cl2–Ni2–N6 178.4(2), Cl2–Ni2–N7 81.89(13), Cl2–Ni2–N8 81.17(12), N5–Ni2–N6 83.2(2), N5–Ni2–N7 83.4(2), N5–Ni2–N8 81.6(2), N6–Ni2–N7 99.1(2), N6–Ni2–N8 98.2(2), N7–Ni2–N8 155.5(2), Ni1–Cl1–Ni2 99.87(6), Ni1–Cl2–Ni2 87.68(4).

Both amine functions of the *ortho*-phenylenediamine spacer are acting as monodentate donors towards different metal centers. This coordination mode is unusual and to the best of our knowledge has not been observed to date as *ortho*-phenylenediamine normally would be expected to coordinate with both donor functions to one metal center with formation of a stable five-membered ring.

The rigid aromatic spacer enforces a rather short distance between the two Ar-NH amine functions which leads to a nonplanar central $Ni(\mu\text{-}Cl)_2Ni$ ring which is folded along the Cl1–Cl2 vector. The N3–Ni1–N4 (N7–Ni2–N8) angles of 157.0(2)° [155.5(2)°] deviate most notably form the linear arrangement expected for octahedral coordination. This type of bending allows for an interaction of the protons at N3, N4, N7, and N8 with the bridging chlorido ligand Cl2 (range of N···Cl2 distances 3.097–3.156 Å). This interaction in turn leads to significantly different Ni–Cl1 [Ni1–Cl1 2.358(2) Å, Ni2–Cl1 2.334(2) Å] and Ni–Cl2 [Ni1–Cl2 2.5769(15) Å, Ni2–Cl2 2.6069 (14) Å] separations and two different Ni–Cl–Ni angles [Ni1–Cl1–Ni2 99.87(6)°, Ni1–Cl2–Ni2 87.68(4)°]. This type of distortion has not been observed in dichlorido-bridged dinickel complexes with unbridged tripodal tetraamines where symmetrical Ni–Cl distances of about 2.46 Å have been observed.[11] However, similar intramolecular O–H···Cl hydrogen bonds have been been observed in a series of dinickel complexes with pyrazolato-bridged octaamine ligands.[3d]

The complex trication of **6**·CH_3CN (Figure 2) contains two zinc centers, each pentacoordinated by four amine functions of a tripodal unit and the bridging fluorido ligand. Only a few examples of such a bridging coordination mode of a fluorido ligand to two zinc centers in discrete complexes are known.[10b] As observed for the nickel complex **5** each of the Ar-NH amine functions is coordinated in a monodentate fashion to one metal center. The coordination geometry of both metal atoms is best described as trigonal-bipyramidal with τ values[13] of 0.79 (Zn1) and 0.87 (Zn2). This coordination geometry is typical for Zn^{II} complexes with tripodal ligands[14] although exceptions have been described.[15] The tertiary amine function and the fluorido ligand occupy the axial positions in the trigonal bipyramid. In accord with previous observation the $Zn–N_{tert}$ bonds [Zn–N1 2.168(3) Å, Zn–N5 2.174(3) Å] are slightly longer than the Zn–N bonds involving the secondary amines.[16]

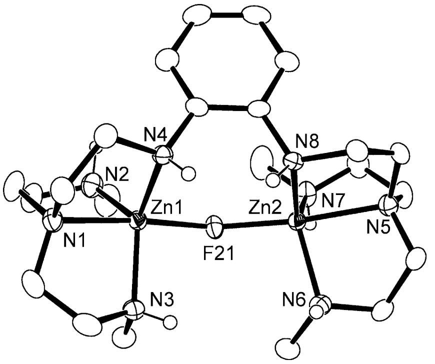


Figure 2. Molecular structure of the complex trication in **6**·CH_3CN (C–H protons have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Zn1–F21 1.968(2), Zn1–N1 2.168(3), Zn1–N2 2.074(3), Zn1–N3 2.076(3), Zn1–N4 2.127(3), Zn2–F21 1.966(2), Zn2–N5 2.174(3), Zn2–N6 2.079(3), Zn2–N7 2.069(3), Zn2–N8 2.156(3); F21–Zn1–N1 171.72(11), F21–Zn1–N2 104.00(11), F21–Zn1–N3 91.51(11), F21–Zn1–N4 94.37(10), N1–Zn1–N2 84.18(12), N1–Zn1–N3 83.08(12), N1–Zn1–N4 83.62(11), N2–Zn1–N3 120.64(13), N2–Zn1–N4 111.35(13), N4–Zn1–N4 124.31(12), F21–Zn2–N5 174.32(11), F21–Zn2–N6 101.82(11), F21–Zn2–N7 94.60(11), F21–Zn2–N8 93.34(10), N5–Zn2–N6 83.74(12), N5–Zn2–N7 83.59(12), N5–Zn2–N8 83.15(11), N6–Zn2–N7 119.10(13), N6–Zn2–N8 114.80(11), N7–Zn2–N8 122.29(13), Zn1–F21–Zn2 146.34(12).

Conclusions

We have prepared the dinuclear complexes $[Ni_2(\mu\text{-}Cl)_2(H_6\text{-}\mathbf{4})](BF_4)_2$ (**5**) and $[Zn(\mu\text{-}F)(H_6\text{-}\mathbf{4})](BF_4)_3$ (**6**) with the bis(tripodal) octaamine ligand H_6-**4**. In both complexes the *ortho*-phenylenediamine spacer between the two tripodal units coordinates with the two amine donors to different metal centers, a coordination mode not observed previously for *ortho*-phenylenediamines. Thus, suitably substituted *ortho*-phenylenediamines appear as promising ligands for the generation of dinuclear complexes containing metal centers in close proximity to allow for a cooperative interaction with selected substrates.

Experimental Section

Starting Materials, Reaction Conditions and Instrumentation: Syntheses of complexes as well as the final reduction step in the ligand synthesis were carried out under argon by using Schlenk or glovebox techniques. Bis{2-[(*tert*-butoxycarbonyl)amino]ethyl}-amine (**2**) was synthesized according to a literature procedure.[17] Solvents were dried and freshly distilled prior to use. Elemental analyses were performed with a Vario EL III Elemental Analyzer at the Institut für Anorganische und Analytische Chemie, University Münster.

***N*,*N'*-Bis(bromoacetyl)-*ortho*-phenylenediamine (1):** A sample of *ortho*-phenylenediamine (5.40 g, 50 mmol) was dissolved in thf (200 mL) and treated dropwise with bromoacetyl bromide (10.9 mL, 125 mmol) and triethylamine (21.0 mL, 150 mmol) at 0 °C. The resulting suspension was stirred at ambient temperature for 12 h. During this period a white solid formed, which was collected by filtration. The solid residue was washed with thf, water and again with thf and was then dried in vacuo. Yield: 9.56 g (27.3 mmol, 55%) of a colorless solid. ^{1}H NMR (200.1 MHz, [D$_6$]-dmso, 25 °C): δ = 9.74 (s, 2 H, NH), 7.53 (m, 2 H, Ar-H), 7.20 (m, 2 H, Ar-H), 4.12 (s, 4 H, CH_2) ppm. ^{13}C NMR (50.3 MHz, [D$_6$]-dmso, 25 °C): δ = 165.1 (CO), 130.2 (Ar-C_{ipso}), 125.5, 124.9 (Ar-C), 30.2 (CH_2) ppm. MALDI-MS (positive ions): *m/z* = 351 $[M + H]^+$, 269 $[M - Br]^+$. $C_{10}H_{10}Br_2N_2O_2$ (350.01): calcd. C 34.32, H 2.88, N 8.00; found C 34.43, H 2.90, N 7.97.

***N*,*N'*-Bis[(bis{2-[(*tert*-butoxycarbonyl)amino]ethyl}amino)acetyl]-*ortho*-phenylenediamine (3):** Compound **2** (15.15 g, 50 mmol) was dissolved in ethyl acetate (80 mL), and **1** (7.55 g, 25 mmol), potassium carbonate (10.35 g, 75 mmol) and water (10 mL) were added. The reaction mixture was heated under reflux for 12 h. The solvents were removed in vacuo. The residue was taken up in water (50 mL) and extracted twice with dichloromethane (50 mL each). The combined organic layers were dried with anhydrous sodium sulfate and filtered. Removal of the solvent in vacuo gave a white solid. Yield: 13.34 g (16.8 mmol, 67%). ^{1}H NMR (400.0 MHz, $CDCl_3$, 25 °C): δ = 9.67 (s, 2 H, Ar-NH), 7.46 (m, 2 H, Ar-H), 7.09 (m, 2 H, Ar-H), 5.55 (s, 4 H, NH-Boc), 3.18 (m, 12 H, NCH_2CO and NCH_2CH_2NHBoc), 2.56 (t, 8 H, NCH_2CH_2NHBoc), 1.29 (s, 36 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 170.4 (ArNHCO), 156.4 [NHC(O)O], 129.7 (Ar-C_{ipso}), 125.6, 124.8 (Ar-C), 79.0 [$C(CH_3)_3$], 60.0 (NCH_2CO), 55.5 (NCH_2CH_2NHBoc), 38.4 (NCH_2CH_2NHBoc), 28.2 (CH_3) ppm. MALDI-MS (positive ions): m/z = 795 $[M + H]^+$, 817 $[M + Na]^+$, 833 $[M + K]^+$. $C_{38}H_{66}N_8O_{10}$ (794.99): calcd. C 57.41, H 8.37, N 14.10; found C 57.44, H 8.33, N 14.14.

Ligand H_6-4: Lithium aluminum hydride (0.91 g, 24.0 mmol) was suspended in dry thf (100 mL). To this suspension was added dropwise a solution of **3** (1.91 g, 2.4 mmol) in dry thf (20 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h and subsequently heated under reflux for 12 h. After cooling to 0 °C, the reaction was quenched by dropwise addition of water (1.8 mL). The precipitate, which had formed, was removed by filtration. The solution obtained was dried with anhydrous sodium sulfate, filtered, and the solvent was removed in vacuo. Ligand H_6-**4** was obtained as a colorless oil, which could be used without further purification. Yield: 0.80 g (1.9 mmol, 79%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 6.70 (m, 2 H, Ar-H), 6.59 (m, 2 H, Ar-H), 3.15 (t, 4 H, NCH_2CH_2NHAr), 2.70 (t, 4 H, NCH_2CH_2NHAr), 2.58 (m, 16 H, $NCH_2CH_2NHCH_3$), 2.34 (s, 12 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 136.9 (Ar-C_{ipso}), 118.6, 111.2 (Ar-C), 54.0 ($NCH_2CH_2NHCH_3$), 53.5 (Ar-$NHCH_2CH_2N$), 49.6 ($NCH_2CH_2NHCH_3$), 42.1 (Ar-$NHCH_2CH_2N$), 36.3 (CH_3) ppm. MALDI-MS (positive ions): m/z = 423 $[M + H]^+$. $C_{22}H_{46}N_8$ (422.66): calcd. C 62.56, H 10.97, N 26.51; found C 62.52, H 10.92, N 26.53.

$[Ni_2(\mu\text{-}Cl)_2(H_6\text{-}4)](BF_4)_2$ (5): A sample of $Ni(BF_4)_2\cdot 6H_2O$ (580 mg, 1.7 mmol) was dissolved in thf (20 mL), and a solution of H_6-**4** (359 mg, 0.85 mmol) in thf (5 mL) was added. The reaction mixture was stirred at ambient temperature for 1 h. Subsequently, the solvent was separated from the precipitated green oil. The oily residue was dried in vacuo and then dissolved in acetonitrile (20 mL). A solution of tetrabutylammonium chloride (472 mg, 1.7 mmol) in acetonitrile (10 mL) was added, and the reaction mixture was stirred at ambient temperature for 12 h. Then the volume of the solution was reduced to 10 mL, and insoluble compounds were removed by filtration. Addition of diethyl ether (40 mL) to the filtrate caused precipitation of a dark green solid, which was collected by filtraton. The solid was dissolved in methanol. Slow diffusion of diethyl ether into this solution gave green crystals of **5**. Yield: 420 mg (0.54 mmol, 64%). IR (KBr): $\tilde{\nu}$ = 3288 (s), 3019 (w), 2991 (w), 2977 (w), 2931 (w), 2894 (w), 2811 (w), 1491 (m), 1082 (s) cm^{-1}. UV/Vis (methanol): λ = 376 (sh), 605, 996 nm. ESI-MS: m/z = 305.1 $[Ni_2Cl_2(H_6\text{-}4)]^{2+}$.

$[Zn_2(\mu\text{-}F)(H_2\text{-}4)](BF_4)_3$ (6): A sample of 3.2 mL of a 0.5 M solution of tetrafluoroboronic acid (1.6 mmol) in thf was added to a solution of the ligand H_6-**4** (169 mg, 0.4 mmol) in thf (5 mL), which led to precipitation of the salt $(H_{10}\text{-}4)(BF_4)_4$. The solvent was decanted, and the remaining solid was dried in in vacuo. The salt was suspended in thf (15 mL), and 0.8 mL of a 1 M solution of diethylzinc (0.8 mmol) in hexane was added. Acetonitrile (10 mL) was added, and the resulting solution was stirred at ambient temperature for 12 h. The volume of the solution was reduced in vacuo to 3 mL. Subsequently, thf (80 mL) and diethyl ether (80 mL) were added, which led to precipitation of a colorless solid. This solid was collected by filtration and dried in vacuo. Crystals of **6**·CH_3CN suitable for an X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a solution of complex **6** in acetonitrile. Yield: 273 mg (0.33 mmol, 83%) of a colorless crystalline solid. ^{1}H NMR (400.0 MHz, CD_3OD, 25 °C): δ = 7.42 (m, 4 H, Ar-H), 3.63–2.65 (br. m, 24 H, CH_2, CH_3) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, 25 °C): δ = 138.8, 126.7, 119.6 (Ar-C), 53.3, 53.2, 52.4, 51.6, 51.0, 50.1, 48.3, 47.8, 46.8, 45.9, 45.7 (CH_2), 36.4 (CH_3) ppm. ^{19}F NMR (376.4 MHz, CD_3OD, 25 °C): δ = –153.2 (BF_4^-), –157.7 (ZnFZn) ppm. IR (KBr): $\tilde{\nu}$ = 3300 (m), 2977 (w), 2936 (w), 2885 (w), 1626 (m), 1479 (m), 1078 (s) cm^{-1}. ESI-MS: m/z = 190.4 $[Zn_2F(H_6\text{-}4)]^{3+}$, 285.1 $[\{Zn_2F(H_6\text{-}4)\} - H]^{2+}$.

X-ray Diffraction Studies: Diffraction data for **5** and **6**·CH_3CN were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K by using graphite-monochromated Mo-K_a radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[18] program package. Structures were solved with the SHELXTL-97[19] package by using the heavy-atom method and were refined with SHELXL-97[20] against $|F^2|$, first with isotropic and later with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions. CCDC-739841 (**5**) and CCDC-739842 (**6**·CH_3CN) 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.

Crystal Data for $[Ni_2(\mu\text{-}Cl)_2(H_6\text{-}4)](BF_4)_2$ (5): $C_{22}H_{46}N_8B_2Cl_2F_8Ni_2$, M = 784.61, monoclinic, $P2_1/n$, Z = 4, a = 11.9537(8), b = 19.1882(12), c = 15.0134(10) Å, β = 109.2330(10)°, V = 3251.4(4) Å^3, 28661 measured reflections, 6401 unique reflections (R_{int} = 0.1268), R = 0.0557, wR = 0.1041 for 3443 contributing reflections [$I \geq 2\sigma(I)$], refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms in calculated positions.

Crystal Data for $[Zn_2(\mu\text{-}F)(H_6\text{-}4)](BF_4)_3\cdot CH_3CN$ (6·CH_3CN): $C_{24}H_{49}N_9B_3F_{13}Zn_2$, M = 873.89, triclinic, $P\bar{1}$, Z = 2, a = 9.0243(4), b = 12.4647(5), c = 16.3701(7) Å, α = 93.7990(10), β = 94.2920(10), γ = 93.8580(10)°, V = 1827.36(13) Å^3, 18309 measured reflections, 8403 unique reflections (R_{int} = 0.0320), R = 0.0504, wR = 0.1266 for 6256 contributing reflections [$I \geq 2\sigma(I)$], refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions.

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