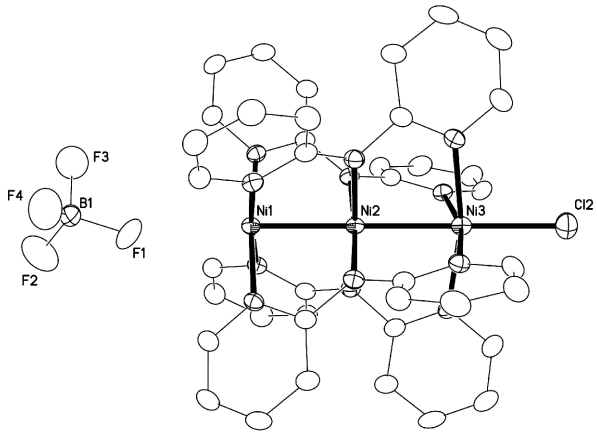
Preparation of $Ni_3(dpa)_4Cl(BF_4)$

To a mixture of 281 mg (0.303 mmol) of $Ni_3(dpa)_4Cl_2$ and 185 mg (0.637 mg) of $TlBF_4$ was added 20 mL of dichloromethane. The mixture was stirred for 1 h and became red with white precipitate. The solution was filtered with the aid of Celite, and was layered with hexanes. Crystals of $Ni_3(dpa)_4Cl(BF_4)\cdot CH_2Cl_2$ grew in a week.

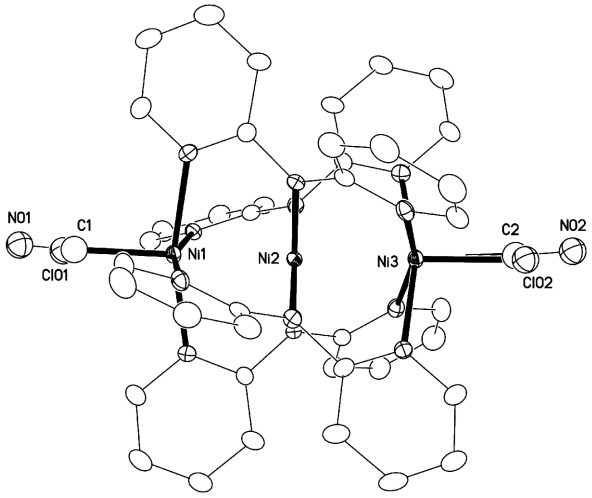
$Ni_3(dpa)_4Cl(BF_4)\cdot CH_2Cl_2$ Crystal data: $C_{41}H_{34}BCl_3F_4N_{12}Ni_3$, M = 1064.09, monoclinic, *a* = 18.699(1), *b* = 16.994(1), *c* = 15.598(1) Å, β = 110.714(1)°, *V* = 4636.1(6) Å^3, T = 213 K, space group *C*2/*c*, *Z* = 4.



Preparation of $Ni_3(dpa)_4(CN)_xCl_{2-x}$

A mixture of 150 mg (0.162 mmol) of $Ni_3(dpa)_4Cl_2$ and 317 mg (6.47 mmol) of NaCN dissolved in 20 mL of 1:1 (v:v) methanol/acetone was stireed for 20 h. The solvent was then removed under vacuum, and the residues were extracted with 10 mL of dichloromethane, giving a red-purple solution which was filtered and layered with hexanes. Crystals of $Ni_3(dpa)_4(CN)_xCl_{2-x}\cdot yCH_2Cl_2$ grew within a week. Yield: 127 mg, 86%.

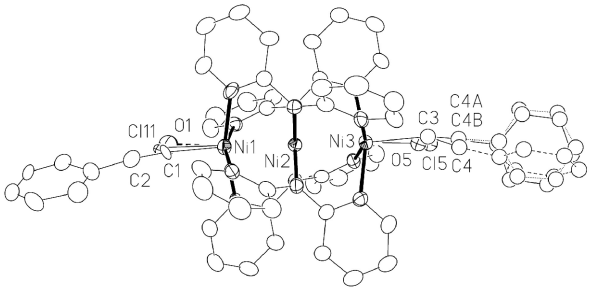
$Ni_3(dpa)_4(CN)_xCl_{2-x}$. Crystal data: $C_{43.38}H_{32}N_{13.72}Ni_3Cl_{2.75}$, M = 944.4, monoclinic, *a* = 37.306(2), *b* = 16.2349(9), *c* = 22.481(1) Å, β = 109.120(1)°, *V* = 12864(4) Å^3, T = 213 K, space group *C*2/*c*, *Z* = 12.



Preparation of $Ni_3(dpa)_4(CCPh)_x(OH)_yCl_{2-x-y}$

A methanol solution (5 mL) of phenyl acetylene (36 μL, 0.32 mmol) and sodium hydroxinde (13 mg, 0.32 mmol) was added to a methanol solution (15 mL) of $Ni_3(dpa)_4Cl_2$. The resulting dark purple solution was stirred for 20 h. The solvent was then removed by vacuum and the residue was extracted with 3 mL of dichloromethane. The resulting solution was filtered and layered with hexanes giving crystals of $Ni_3(dpa)_4(CCPh)_x(OH)_yCl_{2-x-y}\cdot zCH_2Cl_2$ in 5% yield.

$Ni_3(dpa)_4(CCPh)_x(OH)_yCl_{2-x-y}$. Crystal data: $C_{52.21}H_{41.91}N_{12}Ni_3Cl_{2.84}O_{0.46}$, M = 1121.61, monoclinic, *a* = 21.34(1), *b* = 15.237(8), *c* = 18.21(1) Å, β = 111.41(5)°, *V* = 5514(5) Å^3, T = 213, space group $P2_1/c$, *Z* = 4.



Preparation of $Ni_3(dpa)_4(CCPh)_xCl_{2-x}$

To a mixture of 100 mg (0.108 mmol) of $Ni_3(dpa)_4Cl_2$ and 76 mg (0.216 mmol) of $TlPF_6$ was added 25 mL of the methanol. The purple mixture was stirred, and 216 μL of a 1 M NaOH solution in methanol was added. The mixture became red-purple, and a white precipitate was observed. The mixture was stirred for 10 min. and filtered. To the filtrate was added 200 μL of phenylacetylene. Upon standing overnight, crystals grew from this solution.

$Ni_3(dpa)_4(CCPh)_xCl_{2-x}$. Crystal data: $C_{53.92}H_{41.78}N_{12}Ni_3Cl_{0.30}O_{0.32}$, M = 1049.70, monoclinic, *a* = 37.077(3), *b* = 15.878(1), *c* = 17.153(1) Å, β = 92.535(1)°, *V* = 10088(1) Å^3, T = 213 K, space group *C*2, *Z* = 8.