A trimetal chain cocooned by two heptadentate polypyridylamide ligands

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Compounds of nickel in which a chain of three metal atoms is closely embraced by two interlocking heptadentate dianions derived from a chain of five pyridyl groups linked at the 2, or 2 and 6, positions by four amide nitrogen atoms are reported. This new type of extended metal atom chain (EMAC) compound differs from earlier ones in that ligand exchange at the axial positions cannot occur, because the axial ligands are part of the entire ligand. Four such compounds, all crystallographically characterized, are reported. This work is a *proof-of-concept* project that will be extended to other metals with these and other homologous ligands.

Introduction

The field of extended metal atom chain (EMAC) compounds began in 1968 when $Ni_3(dpa)_4Cl_2$ was reported,[1] but did not develop at all, even when the correct structure, Fig. 1, for this compound was recognized.[2] It was not until the very last years of the twentieth century that extensive work in several laboratories[3,4] began to reveal the breadth and fascination of the field.[5] Two major lines of experimental development have been: (1) the extension to other metals, *i.e.*, Cr, Co, Cu, Ru and Rh, and (2) the lengthening of the metal atom chains by the use of longer polypyridylamide ligands. There have also been some significant theoretical efforts to elucidate the electronic structures,[6] but these molecules are difficult to treat rigorously. One of the most seductive characteristics of the EMACs that have been reported so far is their structural resemblance to an ordinary, everyday electrical wire, but on the smallest possible scale. For EMACs to function as molecular scale wires it must be possible to connect them at each end into molecular scale circuits. From this point of view, the fact that all EMACs to date have had axial positions where anions or other donors could be attached must be viewed as an asset. On the other hand, the lability of axial ligands can be a disadvantage in some circumstance, such as when an oxidation is accompanied by a change of axial ligands.[7]

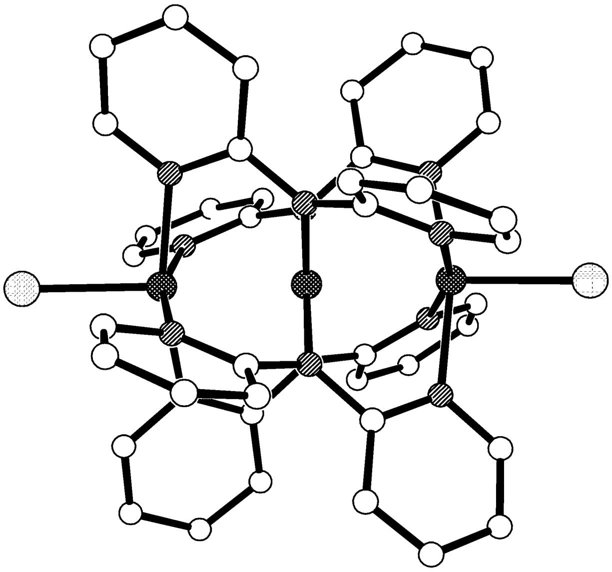

Fig. 1 Structure of $Ni_3(dpa)_4Cl_2$ (dpa = *N*,*N*′-dipyridylamide).

We considered that a way to avoid this might entail combining two of the polypyridyl ligands that run along the metal atom chain and one of the axial ligands into one continuous chain of donor atoms. Our work so far is a *proof-of-concept* project, in which we have shown that the desired type of ligand can be synthesized and EMACs cocooned inside the ligands can be made, with nickel as the first metal to be used.

Results and discussion

Ligand syntheses

Several years ago, the ligand **I** (Chart 1) was reported along with a linear nonanickel EMAC,[8] but the methods of preparation were not (and so far as we know never have been) presented in the literature. The trivial name and abbreviation proposed for this ligand prior to deprotonation were pentapyridyl tetramine, H_4peptea. To avoid unnecessarily complicating the literature, we shall continue to use this trivial name and its abbreviation. We have now made H_4peptea-type ligands with alkyl substituents (**II** and **III**) and their trimetal complexes by the route shown in Scheme 1, which also shows how the compounds are numbered. The synthetic details are given in the experimental section but it should be noted that no species with nuclearity higher than three were isolated nor observed in the mass spectra. A previous preparation of **2** in which Bu^tOK was used as the base gave only an 8% yield.[9] None of the H_4peptea derivatives shown in Scheme 1 have been reported before.

Syntheses of trinickel compounds

The preparation of the trimetal complexes was carried out in refluxing diglyme. The ligand was deprotonated by methyllithium and nickel chloride then added in the stoichiometric amount. It

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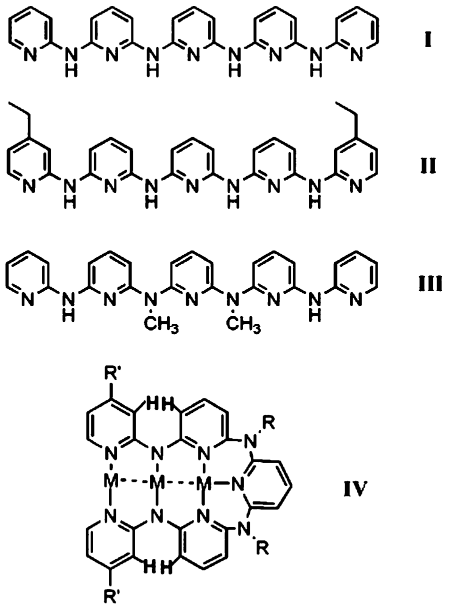
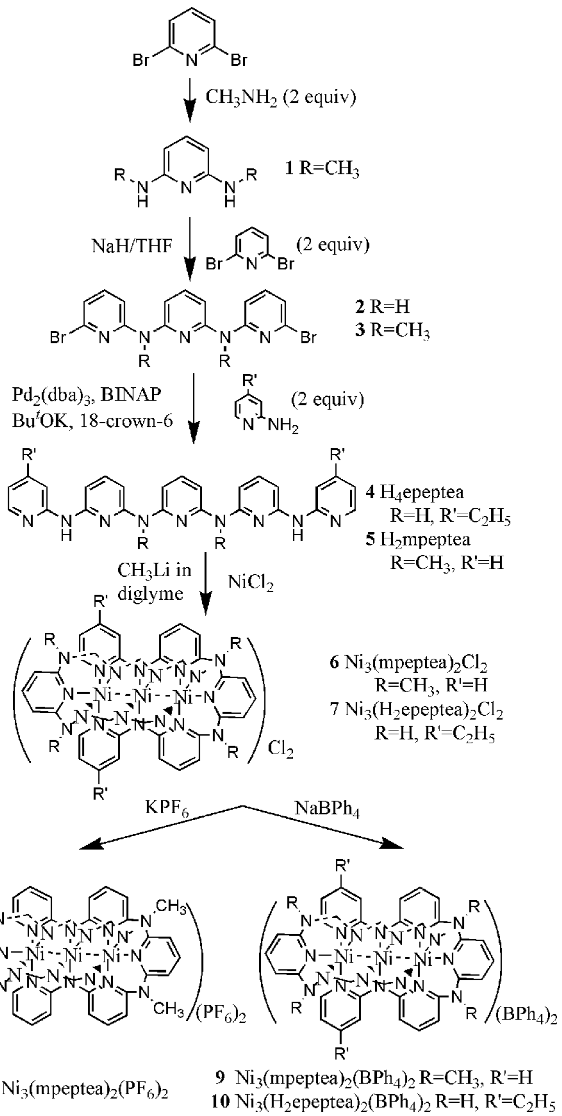


Chart 1

is necessary to have extremely dry $NiCl_2$, THF and diglyme. For optimum results, the $NiCl_2$ must be refluxed in thionyl chloride and the solvent diglyme must be refluxed with Na/K (1/3) overnight prior to use. It has been found that high temperature is necessary to obtain these trinickel EMACs. To subsequently replace the chloride ions, KPF_6 and $NaBPh_4$ were used in CH_2Cl_2, from which NaCl and KCl precipitated. The desired products remained in solution, from which they could be crystallized by layering with isomeric hexanes.

Crystal structures

Crystallographic studies have shown that it is possible to lock in donor atoms at the axial positions of an EMAC by making them part of a large polydentate ligand that runs up one side and down the other of the central metal atom chain, as shown simplistically in **IV**. This is an artificially flattened representation of one heptadentate ligand together with three metal atoms that it can embrace. When another such ligand is introduced in a plane perpendicular to the one shown, and oppositely oriented, each metal atom becomes fully coordinated and a stable compound results in which the trimetal unit is cocooned. In this type of molecule each ligand is twisted to form a capped helix in order to relieve repulsion between the hydrogen atoms shown in bold in **IV**.



Scheme 1 The synthetic routes for preparation of the ligands and trinickel complexes.

Selected bond distances and angles for compounds **7**, **8**, **9**, **10** are listed in Table 1. For the compound $[Ni_3(H_2epeptea)_2]Cl_2$, **7**, which has two ethyl-substituted ligands (**4**) there are two

Table 1 Selected bond distances (Å) and angles (°)

	7·$4CH_3OH·0.5H_2O$[a]	**8**·$0.75C_3H_6O·0.5H_2O$[a]	**9**·$3C_3H_6O$	**10**·$3CH_2Cl_2$
Ni1 · · · Ni2	2.378(2)	2.343(1)	2.3527(9)	2.382(1)
Ni2 · · · Ni3	2.382(2)	2.347(1)	2.3560(9)	2.386(1)
Ni_{outer}–$N_{(av)}$	2.056[9]	2.065[5]	2.057[4]	2.068[6]
Ni_{inner}–$N_{(av)}$	1.885[8]	1.887[6]	1.888[5]	1.888[7]
Ni–$N_{axial\ (av)}$	1.990[9]	1.978[8]	1.986[6]	2.015[9]
Ni1 · · · Ni2 · · · Ni3	178.57(7)	179.54(5)	179.26(4)	178.96(6)
N14–Ni1 · · · Ni2	179.2(2)	178.8(2)	179.2(1)	179.2(2)
N5–Ni3 · · · Ni2	178.3(2)	179.7(2)	179.6(1)	179.2(2)

[a] Only data for one of the two crystallographically independent molecules in **7** and **8** are provided because they are very similar.

crystallographically independent, but chemically equivalent molecules. This compound crystallizes in the monoclinic space group $P2_1/c$, and the structure of the cation is shown in Fig. 2. The Ni···Ni separations in one of the independent molecules are 2.378(2), and 2.382(2) Å and similar to those in the other molecule. The Ni···Ni···Ni unit is essentially linear, having an angle of 178.57(7)°. The coordination about the Ni atoms differs depending on whether they are at the outer edges of the molecular wire, or inside the wire. The former are square pyramidal while the latter is square planar. Because of such difference in coordination, the average Ni–N bond length on the central nitrogen atom is ~0.17 Å shorter than those for the outer Ni atoms. For the terminal Ni atoms, the axial Ni–N bond length is ~0.07 Å shorter than the equatorial Ni–N bond lengths. Compound **10**, which also crystallizes in the monoclinic space group $P2_1/c$, has the same cation as **7** and differs only in the nature of the anions.

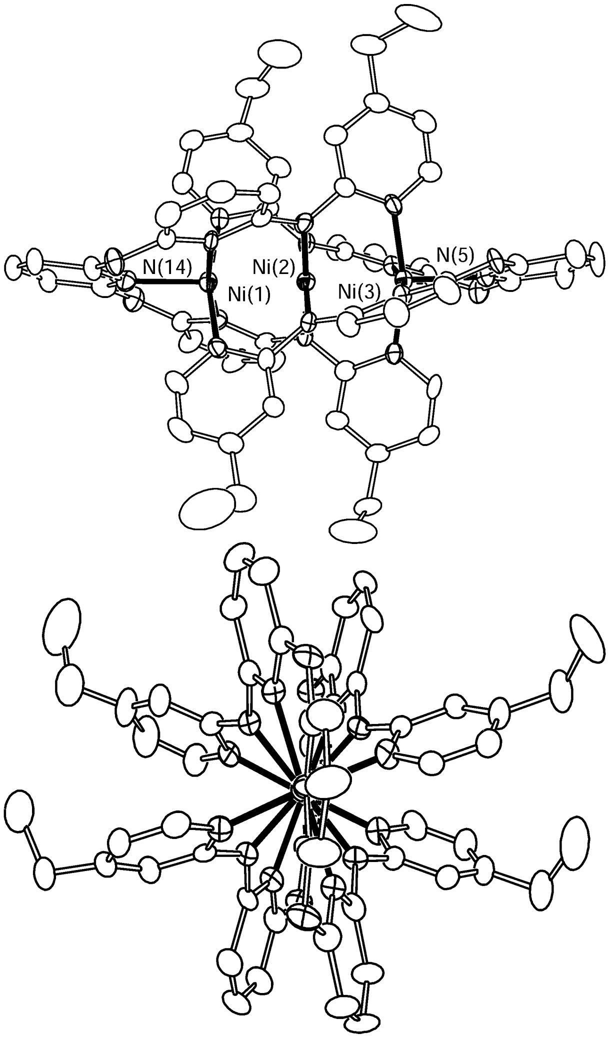


Fig. 2 Side view (top) and end view (bottom) for the cation in $[Ni_3(H_2epeptea)_2]Cl_2$, **7**. Displacement ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity. The cation in **10**, which has tetraphenylborate counter-anions is similar.

Another pair of salts whose cations are the same, $[Ni_3(mpeptea)_2]^{2+}$, but differ in the nature of the anions is **8** and **9**. The ligand mpeptea is derived from **5** in Scheme 1. Compound **8** has PF_6 anions and crystallizes in the triclinic space group $P\bar{1}$ with two crystallographically independent molecules and **9**, which has BPh_4 anions, crystallizes in the monoclinic space group $P2_1/c$. The structure of the cation in **9** is shown in Fig. 3. The Ni···Ni separations are slightly different in these cations, 2.3527(9) and 2.3560(9) Å for **9** and 2.343(1) and 2.347(1) Å for one of the crystallographically independent molecules in **8**. It is noteworthy that the latter are the shortest separations between nickel atoms among all Ni_3^{6+} species reported to date. Though these distances are rather short, no bond is expected between the nickel atoms.

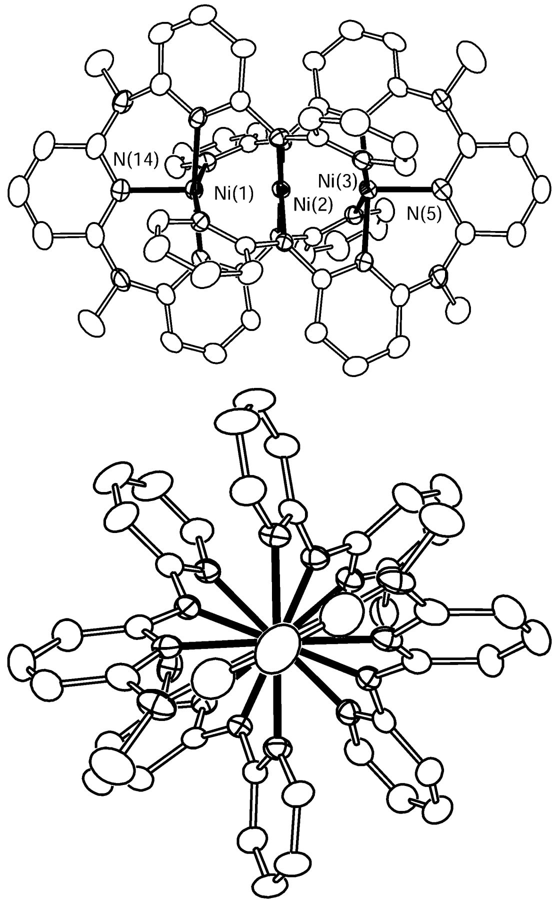


Fig. 3 Side view (top) and end view (bottom) for the cation in $[Ni_3(mpeptea)_2](BPh_4)_2$, **9**. Displacement ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity. The cation in **8**, which has hexafluorophosphate counter-anions is similar.

In all cocooned compounds (**7–10**), the Ni···Ni···Ni angles are very close to 180°. The trinickel chain is symmetrical, having roughly D_2 symmetry. In comparing the structures of **7–10** with those having $Ni_3(dpa)_4X_2$ units, the most obvious difference is that **7–10** are helically wrapped by only two long chain ligands instead of four dpa ligands.

Conclusion

The concept of having two long, polydentate ligands coordinate to form a protective cocoon around an EMAC has been shown to be feasible in the simplest case, where there are only three metal atoms in the chain, and with nickel as the metal. The ligands and the complexes have been made in respectable yields and on a useful scale. With this *proof-of-concept* successfully completed, there are now two next steps to take. One is to make analogues of the complexes reported here with other metals, such as Cr, Co and Cu, and the other is to try to make EMACs of this new type with five metal atoms in the chain.

Experimental

General procedures

All manipulations were carried out under dry nitrogen using standard Schlenk techniques. All solvents were either distilled over appropriate drying agents in a nitrogen atmosphere or purified by means of a Glass Contour solvent system. Sodium tetraphenylborate was purchased from Strem. Anhydrous nickel chloride, 2,6-dibromopyridine, methylamine (40 wt% solution in water), sodium hydride, 2-aminopyridine, bis(2-methoxyethyl) ether, potassium hexafluorophosphate, $Pd_2(dba)_3$, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), 18-crown-6, Bu^tOK and methyllithium (1.6 M in diethyl ether) were purchased from Aldrich Chemical Co.; methylamine was diluted to 25 wt% with water before use, and anhydrous nickel chloride, 2,6-dibromopyridine, sodium tetraphenylborate and potassium hexafluorophosphate were dried overnight under dynamic vacuum at 70 °C prior to use. Other chemicals were used as received; 2-amino-4-ethylpyridine was prepared according to a published method.[10]

Physical measurements

^1H NMR spectra were obtained on a Mercury 300 NMR spectrometer with chemical shifts referenced to DMSO (δ = 2.49 ppm). The ^{19}F NMR spectrum was obtained on an Inova 300 NMR spectrometer ($CFCl_3$, $\delta = 0.0$ ppm). Mass spectrometry data were recorded at the Laboratory for Biological Mass Spectrometry at Texas A & M University. UV-vis spectra were measured on a Shimadzu UV-2501PC spectrophotometer in dichloromethane solutions. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ.

Synthesis of 2,6-dimethylaminopyridine, 1. This compound was made by a modification of a literature procedure.[11] A mixture of 2,6-dibromopyridine (9.48 g, 40.0 mmol) and a 25% aqueous solution of methylamine (200 mL, 160 mmol) was sealed in a pressure reactor (Parr bomb) under a nitrogen atmosphere, and heated at 190 °C for 10 h. The reaction mixture was cooled to room temperature, diluted with 150 mL of water, filtered, and then 50 mL of 40% NaOH solution was added to the mixture to neutralize the acid. Petroleum ether was used to extract the product from the aqueous solution (4 × 250 mL). The ether extracts were combined and dried over anhydrous K_2CO_3. The solvent was removed under reduced pressure and the white needle solid was collected. Yield: 2.87 g, 52%. ^1H NMR (DMSO-d_6, 300 MHz, δ): 7.04 (t, 1H), 5.83 (q, 2H), 5.54 (d, 2H), 2.67 (d, 6H).

Synthesis of *N*,*N*′-bis(6′-bromopyrid-2′-yl)-2,6-diaminopyridine, 2. A solution of 2,6-diaminopyridine (2.18 g, 20.0 mmol) in THF (30 mL) was added to a suspension of NaH (1.51 g, 60.0 mmol) in THF (30 mL), and the mixture stirred for 30 min. A solution of 2,6-dibromopyridine (14.2 g, 60.0 mmol) in THF (60 mL) was added to give a greenish grey suspension, which was refluxed at 70 °C under a nitrogen atmosphere for 36 h, resulting in a brown solution. After cooling to room temperature, the solution was filtered and the solvent was removed under reduced pressure. The residue was further washed with NH_4Cl solution and CH_2Cl_2. The grey solid was collected on a frit and air-dried. Yield: 4.04 g, 48%. ^1H NMR (DMSO-d_6, 300 MHz, δ): 9.86 (s, 2H), 7.86 (d, 2H), 7.58 (t, 3H), 7.06 (d, 2H), 7.03 (d, 2H). ESI^+ (m/z): 421.8 $[M + H]^+$.

Synthesis of *N*,*N*′-bis(6′-bromopyrid-2′-yl)bismethyl-2,6-diaminopyridine, 3. A solution of 2,6-dimethylaminopyridine (1.37 g, 10.0 mmol) in THF (20 mL) was added to a white suspension of NaH (0.76 g, 30.0 mmol) in THF (20 mL). After stirring for 30 min, 2,6-dibromopyridine (7.11 g, 30.0 mmol) in THF (40 mL) was transferred by cannula to give a grey–white suspension, which was refluxed at 70 °C under a nitrogen atmosphere for 36 h, resulting in a brown suspension. After cooling to room temperature, the solvent was removed under reduced pressure to give a pale brown oil. Addition of isomeric hexanes (50 mL) to the oil precipitated a pale yellow product. After washing with water (3 × 50 mL) and hexanes (3 × 50 mL), the pale yellow solid was collected on a frit. Yield: 3.12 g, 69%. ^1H NMR (DMSO-d_6, 300 MHz, δ): 7.71 (t, 1H), 7.53 (t, 2H), 7.23 (d, 2H), 7.10 (d, 2H), 6.94 (d, 2H), 3.44 (s, 6H). Mass spectrum, ESI^+ (m/z): 450.0 $[M + H]^+$.

Synthesis of *N*,*N*′-bis[6′-(4″-ethylpyrid-2″-yl)aminopyrid-2′-yl]-2,6-diaminopyridine (H_4epeptea), 4. *N*,*N*′-Bis(6′-bromopyrid-2′-yl)-2,6-diaminopyridine (1.68 g, 4.0 mmol) and $Pd_2(dba)_3$ (0.13 g, 12 mol %) in dry benzene (60 mL) were placed in a 250 mL round-bottom flask, and the mixture was stirred for 30 min. Then 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP, 0.152 g, 24 mol %), 18-crown-6 (2.11 g, 8.0 mmol) and Bu^tOK (2.24 g, 20.0 mmol) in dry benzene (30 mL) were added to the reaction mixture by cannula. After stirring for another 30 min, 2-amino-4-ethylpyridine (1.46 g, 12.0 mmol) in dry benzene (10 mL) was added. The resulting mixture was stirred and refluxed at 80 °C under a nitrogen atmosphere for 3 days. The reaction mixture was cooled to room temperature and then quenched with NH_4Cl (2.04 g) in aqueous solution (20 mL). Two phases separated. The organic phase was saved, and the aqueous phase was extracted twice with chloroform (2 × 30 mL). The extracts were combined and dried over $MgSO_4$, and the solvent was removed under vacuum to give the crude product as a black–red oil, which was further purified by column chromatography over silica gel (hexanes–ethyl acetate, 3 : 2). The solvent was removed under reduced pressure, giving a grey powder. Yield: 0.54 g, 27%. ^1H NMR (DMSO-d_6, 300 MHz, δ): 9.28 (s, 2H), 9.05 (s, 2H), 8.09 (d, 2H), 7.67 (s, 2H), 7.50 (t, 3H), 7.33 (d, 2H), 7.18 (d, 2H), 7.13 (d, 2H), 6.75 (d, 2H), 2.61–2.55 (q, 4H), 1.18 (t, 6H). Mass spectrum, ESI^+ (m/z): 504.3 $[M + H]^+$.

Synthesis of *N*,*N*′-bis[(6′-pyrid-2″-yl)aminopyrid-2′-yl]bismethyl-2,6-diaminopyridine (H_2mpeptea), 5. *N*,*N*′-Bis(6′-bromopyrid-2′-yl)bismethyl-2,6-diaminopyridine (1.80 g, 4.0 mmol) and $Pd_2(dba)_3$ (0.13 g, 12 mol %) in dry benzene (60 mL) were placed in a 250 mL round-bottom flask and the mixture was stirred for 30 min. To this mixture 2,2′-bis (diphenylphosphino)-1,1′-binaphthyl (BINAP, 0.15 g, 24 mol %), 18-crown-6 (2.11 g, 8.0 mmol) and Bu^{t}OK (2.24 g, 20.0 mmol) in dry benzene (30 mL) were added to the reaction mixture by cannula. After stirring for another 30 min, 2-aminopyridine (1.13 g, 12.0 mmol) in dry benzene (10 mL) was added. The resulting mixture was stirred and refluxed at 80 °C under a nitrogen atmosphere for 3 days. After cooling to room temperature, the reaction mixture was quenched with NH_4Cl (2.04 g) aqueous solution (20 mL). Two phases were formed. The organic phase was saved, and the aqueous phase was extracted twice with chloroform (2 × 30 mL). The combined extracts were dried over $MgSO_4$, and the solvent was then evaporated under vacuum to give a black–red oil, which was further purified by column chromatography over silica gel (hexanes–ethyl acetate, 3 : 2, with CH_2Cl_2 5%). The solvent was then removed and a pale yellow powder was obtained. Large crystals were obtained by slow evaporation of a CH_2Cl_2 solution of the product. Yield: 0.43 g, 23%. Anal. Calc. for $C_{27}H_{26}N_9O$ (H_2mpeptea·H_2O): C, 65.82; H, 5.32; N, 25.60%. Found: C, 65.92; H, 4.83; N, 25.88%. ^{1}H NMR (DMSO-d$_6$, 300 MHz, δ): 9.52 (s, 2H), 8.19 (d, 2H), 7.75 (d, 2H), 7.61–7.51 (m, 5H), 7.20 (d, 2H), 6.83 (t, 2H), 6.74 (t, 4H), 3.51 (s, 6H). Mass spectrum, ESI$^+$ (*m*/*z*): 476.2 $[M + H]^+$.

Preparation of [Ni$_3$(mpeptea)$_2$]Cl$_2$, 6. *N*,*N*′-Bis[(6′-pyrid-2″-yl)aminopyrid-2′-yl]bismethyl-2,6-diaminopyridine (H_2mpeptea, 0.19 g, 0.40 mmol) was dissolved in 15 mL of THF to give a pale yellow solution. This solution was cooled in a dry ice/acetone bath, and 0.5 mL of 1.6 M MeLi in diethyl ether (0.8 mmol) was added slowly. The mixture was allowed to warm to room temperature to give a yellow suspension, which was transferred to a flask containing anhydrous $NiCl_2$ (0.078 g, 0.60 mmol) by cannula. The resulting deep brown suspension was stirred at room temperature for 2 h, and the solvent was removed under vacuum. After addition of 15 mL of bis(2-methoxyethyl) ether (diglyme), the mixture was stirred and refluxed overnight at 180 °C under nitrogen to give a deep purple precipitate. The solvent was decanted and the remaining precipitate was washed with toluene (2 × 10 mL), THF (2 × 10 mL), diethyl ether (2 × 10 mL), hexanes (2 × 10 mL), and then dried under vacuum for 1 h. The crude product was dissolved in methanol and further purified on an aluminum oxide column using methanol–diethyl ether (1 : 1) as the eluent. A purple band was collected and the solvent was removed under vacuum. The complex was then recrystallized from CH_2Cl_2–hexanes. Small deep purple crystals of **6**·CH_2Cl_2·H_2O were formed after one week. Yield: 60 mg, 26%. Anal. Calc. for $C_{55}H_{50}N_{18}Ni_3Cl_4O$ (Ni_3(mpeptea)$_2Cl_2$·CH_2Cl_2·H_2O): C, 50.93; H, 3.99; N, 19.44%. Found: C, 50.74; H, 4.48; N, 19.40%. Mass spectrum, ESI$^+$ (*m*/*z*): 561.1 $[Ni_3(\text{mpeptea})_2]^{2+}$. UV-vis ($CH_2Cl_2$) λ_{max}/nm (ε/M^{-1} cm^{-1}): 556 (1050).

Preparation of [Ni$_3$(H$_2$epeptea)$_2$]Cl$_2$, 7. This compound was synthesized similarly to **6**, and the product was recrystallized from methanol–diethyl ether.

Preparation of [Ni$_3$(mpeptea)$_2$](PF$_6$)$_2$, 8. A flask containing [Ni$_3$(mpeptea)$_2$]Cl$_2$ (30 mg, 0.025 mmol) and a 20% molar excess of KPF_6 (11 mg, 0.06 mmol) was charged with 15 mL of dichloromethane. The suspended solids slowly dissolved, giving a purple solution. The resulting solution was stirred overnight at room temperature, during which time a white precipitate of KCl had formed. This deep purple solution was filtered through Celite to remove KCl. The dichloromethane was removed under vacuum, the remaining dark purple solid was re-dissolved in methanol (3 mL) and further purified on an aluminium oxide column using methanol–diethyl ether (1 : 2) as the eluent. The product was then recrystallized in a mixture of acetone–hexanes (5: 20), producing deep purple plate-like crystals of **8**·0.75C_3H_6O·0.5H_2O after one week. Yield: 32 mg, 88%. Mass spectrum, ESI$^+$ (*m*/*z*): 561.1 $[Ni_3(\text{mpeptea})_2]^{2+}$. ^{19}F NMR (DMSO-d$_6$, 300 MHz): δ = −70.93 ppm (d) (conforming the presence of PF_6^- anions). UV-vis (CH_2Cl_2) λ_{max}/nm (ε/M^{-1} cm^{-1}): 555 (1000).

Preparation of [Ni$_3$(mpeptea)$_2$](BPh$_4$)$_2$, 9. To a mixture of [Ni$_3$(mpeptea)$_2$]Cl$_2$ (60 mg, 0.05 mmol) and an excess of $NaBPh_4$ (40 mg, 0.12 mmol), was added 15 mL of dichloromethane, giving a purple solution. The resulting solution was stirred overnight at room temperature, during which time a white precipitate, presumably NaCl, had formed. This deep purple solution was filtered through Celite. The dichloromethane was removed under vacuum; the remaining dark purple solid was redissolved in methanol (5 mL) and further purified on an aluminum oxide column using methanol–diethyl ether (1 : 2) as the eluent. Large block deep purple crystals of **9**·3C_3H_6O were obtained by slow diffusion of hexanes (20 mL) into an acetone solution of the product (5 mL) within a week. Yield: 79 mg, 82%. Anal. Calc. for $C_{111}H_{104}B_2N_{18}Ni_3O_3$ (Ni_3(mpeptea)$_2$(BPh$_4$)$_2$·3C_3H_6O): C, 68.87; H, 5.32; N, 13.02%. Found: C, 69.09; H, 5.12; N, 13.01%. Mass spectrum, ESI$^+$ (*m*/*z*): 561.1 $[Ni_3(\text{mpeptea})_2]^{2+}$. UV-vis ($CH_2Cl_2$) λ_{max}/nm (ε/M^{-1} cm^{-1}): 555 (950).

Preparation of [Ni$_3$(H$_2$epeptea)$_2$](BPh$_4$)$_2$, 10. This compound was synthesized similarly to **9**, and the product was recrystallized from CH_2Cl_2–hexanes.

X-Ray crystallography

In each case, a suitable crystal attached at the end of a quartz fiber with a small amount of stopcock grease was placed on a goniometer head. X-Ray diffraction data for **5**, **6**·CH_2Cl_2·H_2O, **7**·4CH_3OH·0.5H_2O, **8**·0.75C_3H_6O·0.5H_2O, **9**·3C_3H_6O and **10**·3CH_2Cl_2 were collected at 213 K on a BRUKER SMART 1000 CCD area detector system.[12] Data reduction and integration were performed with the software SAINTPLUS,[13] while the absorption corrections were applied using the program SADABS.[14] All the structures were solved by direct methods and refined using the SHELXL-97 program.[15] In all structures, hydrogen atoms were added at calculated positions based on a riding model. Some interstitial molecules and PF_6^- anions were found to be disordered. Crystal data are given in Table 2. A displacement ellipsoid plot of **5** is given in Fig. 4.

CCDC reference numbers 618416 (**5**), 618417 (**7**·4CH_3OH·0.5H_2O), 618491 (**8**·0.75C_3H_6O·0.5H_2O), 618490 (**9**·3C_3H_6O) and 618418 (**10**·3CH_2Cl_2).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612076h

Table 2 Crystallographic data

	5	**7**·4CH$_3$OH·0.5H$_2$O	**8**·0.75C$_3$H$_6$O·0.5H$_2$O	**9**·3C$_3$H$_6$O	**10**·3CH$_2$Cl$_2$
Formula	$C_{27}H_{25}N_9$	$C_{62}H_{71}Cl_2N_{18}Ni_3O_{4.50}$	$C_{56.25}H_{50.50}F_{12}Ni_3N_{18}O_{1.25}P_2$	$C_{111}H_{104}B_2N_{18}Ni_3O_3$	$C_{109}H_{100}B_2Cl_6N_{18}Ni_3$
M_r	475.56	1387.39	1464.72	1936.88	2072.52
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$Fdd2$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	17.578(3)	21.001(5)	13.986(7)	25.708(5)	23.186(4)
b/Å	25.708(5)	44.077(11)	14.116(7)	15.112(3)	15.723(3)
c/Å	10.673(2)	13.966(3)	31.151(15)	26.789(5)	28.092(4)
α/°	90	90	85.761(8)	90	90
β/°	90	98.094(5)	78.517(8)	109.406(3)	100.041(3)
γ/°	90	90	80.128(9)	90	90
V/Å^3	4823(2)	12799(5)	5933(5)	9816(3)	10084(3)
Z	8	8	4	4	4
T/K	213	213	213	213	213
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
D_c/g cm^{-3}	1.310	1.439	1.656	1.311	1.365
$R1$,[a] $wR2$[b] ($I > 2\sigma I$)	0.0435, 0.1097	0.0755, 0.1718	0.0617, 0.1457	0.0600, 0.1454	0.0929, 0.2216
$R1$,[a] $wR2$[b] (all data)	0.0529, 0.1168	0.1478, 0.2092	0.1109, 0.1767	0.1206, 0.1776	0.1563, 0.2625

[a] $R1 = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

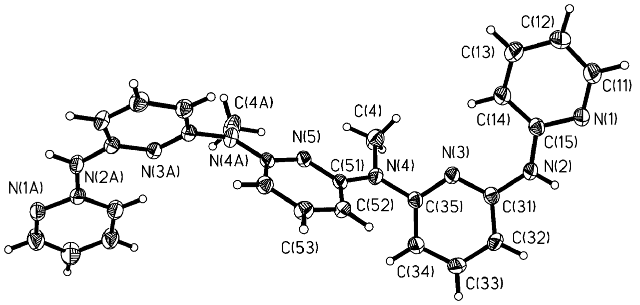


Fig. 4 Structure of compound **5**. Displacement ellipsoids are drawn at the 40% probability level. N(5)–C(51) 1.337(2), N(4)–C(51) 1.393(2), N(4)–C(35) 1.420(2), N(4)–C(4) 1.451(3), N(3)–C(31) 1.334(3), N(3)–C(35) 1.340(2), N(2)–C(31) 1.381(2), N(2)–C(15) 1.393(2), N(1)–C(15) 1.345(3), N(1)–C(11) 1.340(3) Å, N(5)–C(51)–N(4) 114.8(2), N(3)–C(35)–N(4) 115.4(2), N(3)–C(31)–N(2) 119.7(2), N(1)–C(15)–N(2) 112.5(2)°.

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