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Unusual Magnetism of an Unsymmetrical Trinickel Chain

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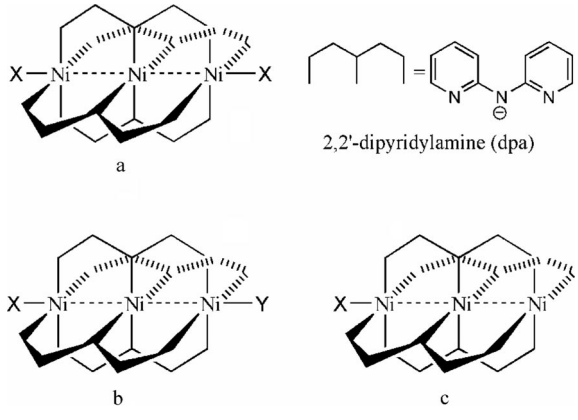
An extended metal atom chain (EMAC) compound with an unsymmetrical trinickel core and the formula $[Ni_3(dpa)_4(CH_3CN)](PF_6)_2 \cdot 2CH_2Cl_2$ (**1**·$2CH_2Cl_2$, dpa is the anion of 2,2′-dipyridylamine) has the central Ni atom in an essentially square-planar configuration. Besides having four equatorial nitrogen atoms, the two terminal metal centers have axial interactions that are notably different with one having a strongly bound acetonitrile molecule with a Ni(3)–N(3) distance of 2.108(5) Å while the other unit has a very weak interaction with an axial PF_6 anion [Ni(1)···F(1) separation of 2.690 Å]. In these outer units, the Ni(3) atom is pulled out of the idealized plane of the four equatorial nitrogen atoms by 0.239 Å, while in the one with an axial PF_6 anion the metal atom is pulled from the plane of the equatorial nitrogen atoms by only 0.097 Å. In **1** there are two unpaired electrons and an $S = 1$ state prevails from ca. 25 to 300 K. This magnetic behavior differs considerably from that of symmetrical trinickel EMACs with two strongly pyramidal terminal nickel atoms. A discussion of the effect of various axial ligands on the geometry of the terminal nickel atoms is provided.

Introduction

Ever since the initial discovery by Aduldecha and Hathaway[1] that the anion of 2,2′-dipyridylamine (dpa) can stabilize linear trinickel coordination compounds, a number of related compounds having the general formula $M_3(dpa)_4X_2$ have been prepared with a variety of metal atoms (M = Cr,[2] Co,[3] Cu,[4] Ru,[5] Rh;[6] X may be a variety of axial ligands such as Cl, Br, CN, PF_6 and so on). These trinuclear compounds are members of the family of compounds referred to as *extended metal atom chains* (EMACs).[7] Compounds of this type with several metal atoms, such as those with nine nickel atoms, have also been reported.[8] In our laboratory an important goal has been the elucidation of their fundamental properties. Several compounds having the formula $Ni_3(dpa)_4X_2$, where X represents different axial ligands, have been synthesized and characterized,[1,9] as well as analogues having Ni_3^{6+} EMACs with the chain closely cocooned by two interlocking heptadentate dianions.[10] Most of the compounds having Ni_3^{6+} units reported thus far have essentially symmetrical structures (Scheme 1, a). While much effort has been placed on understanding axial ligand-exchange processes, less attention has been given to the preparation of less symmetrical species, e.g., those having different ligands on each axial position (Scheme 1, b), or those with an open axial position (Scheme 1, c). The only known unsymmetrical Ni_3^{6+} complex was prepared in very low yield (8%) using the unsymmetrical ligand *N*-phenyl-(2-pyridyl)formamidinate (PhPyF).[11] In $[Ni_3(PhPyF)_4Cl]$-Cl (Scheme 2) the central and one of the outer Ni atoms are essentially square planar but the other outer Ni atom is five-coordinate. The room-temperature magnetic susceptibility showed a magnetic moment of 3.08 μ_B that corresponds to two unpaired electrons, which presumably arise from the terminal five-coordinate unit.



Scheme 1. A simplified representation of EMACs and the polypyridine ligand not showing the characteristic helical twist.

Unsymmetrical species are of interest because axial ligands may influence electronic structures, electrochemistry and magnetic properties of these species[12] and therefore

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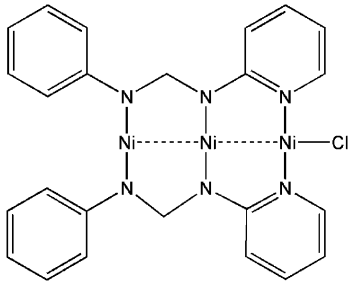


Scheme 2. A portion of the cation $Ni_3(PhPyF)_4Cl^+$ in $[Ni_3(PhPyF)_4Cl]Cl$. There are other two PhPyF ligands perpendicular to the plane, and the central and one of the outer Ni atoms are square planar but the outer Ni atom with the axial chloride group is 5-coordinate; see ref.[11]

provide a way to tune desirable physical properties. Here we report the preparation and structural characterization of a compound, $[Ni_3(dpa)_4(CH_3CN)](PF_6)_2$ (**1**), which was prepared in good yield and study the effect of a weakly coordinated axial ligand on the electronic structure and magnetic properties of this EMAC.

Results and Discussion

Synthesis and Spectral Characterization

The symmetrical starting material $[Ni_3(dpa)_4(CH_3CN)_2](PF_6)_2$,[9e] synthesized by reacting $Ni_3(dpa)_4Cl_2$[13] with two equivalents of $AgPF_6$ in acetonitrile, was used to generate the unsymmetrical target product, $[Ni_3(dpa)_4(CH_3CN)](PF_6)_2$ (**1**), by simply stirring the symmetrical species in dichloromethane at ambient temperature overnight followed by elimination of the solvent under vacuum, in a process that also removed an axial acetonitrile molecule. During the dissolution process in dichloromethane the color of the solution slowly changed from purple to purplish red. Large block-shaped, purplish red crystals of **1**·$2CH_2Cl_2$ were obtained after a layer of hexanes was added to a CH_2Cl_2 solution of the crude product.

Compound **1** is air and moisture stable, readily soluble in CH_2Cl_2 and methanol, and its purity was clearly established by a satisfactory elemental analysis. In addition, ESI mass spectrometry shows only one signal at 428.05 *m*/*z* having the appropriate isotope distribution for the $[Ni_3(dpa)_4]^{2+}$ ion. The electronic spectrum is quite different from those of previously reported trinickel EMACs. The spectrum in dichloromethane solution shows two absorptions, one at 450 nm and another at 520 nm in the visible region but that of $Ni_3(dpa)_4Cl_2$ has only one absorbance at 520 nm. This is consistent with a change in the electronic structure of the Ni_3^{6+} chain upon removal of a strongly bound axial ligand.

It should be noted that attempts to remove the axial acetonitrile molecule by placing **1** under vacuum for prolonged periods of time at room temperature were unsuccessful. If the process was repeated by heating the solid to 130 °C the only isolable products contained $Ni_3(dpa)_4^{2+}$ units with axially coordinated acetamide ligands. Two such compounds were identified, namely $Ni_3(dpa)_4[OC(CH_3)NH]_2$ and a molecule with a chain-like structure, $[Ni_3(dpa)_4(OC(CH_3)NH)]_n$.[14] The acetamide anions presumably form by reaction of acetonitrile with residual hydroxo-containing groups present in the oven-dried glassware. Reactions of acetonitrile with nucleophiles such as water and diphosphanes have been well-documented and are catalyzed by metal centers.[15]

Structural Results

The structure of compound **1**, shown in Figure 1, has the characteristic helical twist of the $Ni_3(dpa)_4^{2+}$ core. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with Z = 4 and two crystallographically independent, but chemically equivalent molecules. The Ni···Ni separations for one of the independent molecules are 2.3396(11) and 2.3548(12) Å, and very similar to those in the other crystallographically independent molecule [2.3450(11) and 2.3651(12) Å] as shown in Table 1. Importantly these Ni···Ni distances are significantly shorter (≈ 0.10 Å) than the corresponding distances of ca. 2.43 Å in $Ni_3(dpa)_4Cl_2$,[13] but only slightly shorter than those in $[Ni_3(dpa)_4(CH_3CN)_2](PF_6)_2$ [2.376(2), 2.371(2) Å].[9e] Even though the Ni···Ni separations in **1** are fairly short, they are still significantly longer than those in the one-electron-oxidized species $[Ni_3(dpa)_4(PF_6)_2]PF_6$ [2.2851(6), 2.289(1) Å] that has a 3-center-1-electron bond[16] or in the ethyl-substituted analogue [2.293(4)Å].[17] For comparison, the Ni···Ni separations for some trinickel compounds are given in Table 2. The Ni···Ni···Ni unit in **1** is essentially linear, having an angle of 179.33(5)°.

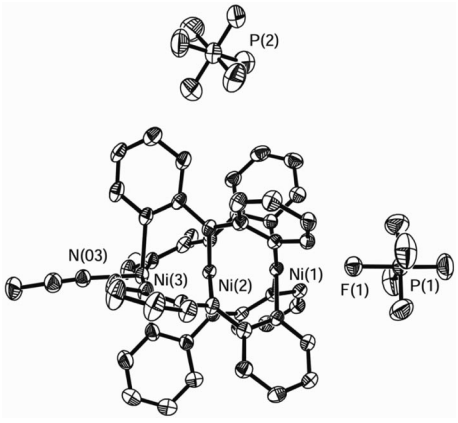


Figure 1. Molecular structure of **1** drawn with ellipsoids at the 40% probability level. All hydrogen atoms have been omitted for clarity. Note that the distance between Ni(1) and F(1) is 2.690 Å while the Ni(3)–N(03) is 2.063(6) Å.

The atom arrangement for each of the three d^8 Ni atoms in **1** is quite different. For each of the crystallographically independent molecules the central unit is nearly square planar[18] and the two termini of the molecule being five-coordinate, square pyramidal. One of the outer Ni atoms has a strongly bound acetonitrile molecule at the apex of the pyramid [Ni(3)–N(03) 2.063(6) Å and Ni(6)–N(06)

Table 1. Selected bond lengths [Å] and angles [°] for the two crystallographically independent molecules in **1**·2CH_2Cl_2.

Bond lengths			
Molecule 1			
Ni(1)···Ni(2)	2.3396(11)	Ni(2)···Ni(3)	2.3548(12)
Ni(1)–N(1)	1.910(5)	Ni(1)–N(4)	1.915(5)
Ni(1)–N(7)	1.912(5)	Ni(1)–N(10)	1.914(5)
Ni(2)–N(2)	1.877(5)	Ni(2)–N(5)	1.878(5)
Ni(2)–N(8)	1.888(5)	Ni(2)–N(11)	1.880(4)
Ni(3)–N(3)	2.108(5)	Ni(3)–N(6)	2.108(5)
Ni(3)–N(9)	2.091(6)	Ni(3)–N(12)	2.089(5)
Ni(3)–N(03)	2.063(6)	Ni(1)···F(1)	2.690
Molecule 2			
Ni(4)···Ni(5)	2.3450(11)	Ni(4)···Ni(5)	2.3651(12)
Ni(4)–N(19)	1.910(5)	Ni(4)–N(16)	1.912(5)
Ni(4)–N(13)	1.913(5)	Ni(4)–N(22)	1.926(5)
Ni(5)–N(14)	1.878(5)	Ni(5)–N(23)	1.884(5)
Ni(5)–N(17)	1.896(5)	Ni(5)–N(20)	1.896(5)
Ni(6)–N(15)	2.099(5)	Ni(6)–N(21)	2.095(6)
Ni(6)–N(18)	2.106(5)	Ni(6)–N(24)	2.099(5)
Ni(6)–N(06)	2.061(6)	Ni(4)···F(7)	2.726
Bond angles			
Ni(1)···Ni(2)···Ni(3)	179.33(5)	N(03)–Ni(3)···Ni(2)	177.90(16)
N(1)–Ni(1)–N(7)	174.1(2)	N(10)–Ni(1)–N(4)	173.5(2)
N(5)–Ni(2)–N(11)	176.8(2)	N(2)–Ni(2)–N(8)	176.4(2)
N(9)–Ni(3)–N(3)	166.0(2)	N(12)–Ni(3)–N(6)	166.6(2)
Ni(4)···Ni(5)···Ni(6)	179.19(4)	N(06)–Ni(6)···Ni(5)	178.70(15)

Table 2. Metal–metal separations for some trinickel EMACs.

Compound[a]	Ni···Ni [Å]	Ref.
$Ni_3(dpa)_4Cl_2$·2CH_2Cl_2	2.4386(9), 2.422(1)	[13]
$Ni_3(dpa)_4(AnCOO)_2$	2.4248(9), 2.4220(9)	[9h]
$Ni_3(dpa)_4(CN)_2$·CH_2Cl_2	2.4523(3)	[9b]
$Ni_3(dpa)_4(N_3)_2$	2.4325(7), 2.4356(7)	[9f]
$[Ni_3(dpa)_4(CH_3CN)_2](PF_6)_2$·3.14$CH_3CN$	2.376(2), 2.371(2)	[9e]
$[Ni_3(PhPyF)_4Cl]Cl$	2.443(3), 2.454(3)	[11]
1	2.3396(11), 2.3548(12) 2.3450(11), 2.3651(12)	this work
$[Ni_3(dpa)_4(PF_6)_2]PF_6$·5$CH_2Cl_2$	2.2851(6), 2.289(1)	[16]
$[Ni_3(depa)_4(PF_6)_2]PF_6$·3$CH_2Cl_2$	2.293[4]	[9e]

[a] Abbreviations: dpa = the anion of 2,2′-dipyridylamine, AnCOO = the anion of antracene-9-carboxylate, PhPyF = the anion of *N*-phenyl-(2-pyridyl)formamidine, depa = the anion of 4,4′-diethyl-2,2′-dipyridylamine.

2.061(6) Å] while the outer has a weakly bound PF_6 anion [Ni(1)···F(1) 2.690 Å and Ni(4)···F(7) 2.726 Å]. These long distances strongly suggest there is very little interaction between the outer Ni^{II} and the fluorine atoms. This is further supported by a comparison of the equatorial Ni–N distances. Those in the central four-coordinate square unit are, as expected,[7] the shortest [range of 1.877(5) to 1.896(4) Å]. For the outer unit bound to the acetonitrile molecule, the corresponding distances are longer by more than 0.2 Å [range of 2.089(5) to 2.108(5) Å]. However, the equatorial Ni–N distances for the site with the hexafluorophosphate anion are only slightly longer than those for the central unit [range of 1.910(5) to 1.926(5) Å].

Interestingly, the outer square-pyramidal units also show important structural differences upon comparison of the distance of the Ni atoms from the idealized square plane formed by the four equatorial nitrogen atoms, shown as *d* in Figure 2. The Ni atom bound to the acetonitrile molecule is pulled 0.239 Å from the plane but that adjacent to the PF_6 anion has a *d* of only 0.097 Å. This difference (vide infra) greatly influences the magnetism. For comparison, the calculated values of *d* for the outer units of other Ni_3^{6+} EMACs are 0.289 and 0.278 Å in $Ni_3(dpa)_4Cl_2$,[17] 0.242 and 0.235 Å in $Ni_3(dpa)_4(CH_3CN)_2$,[9e] 0.238 Å in $Ni_3(depa)_4(CH_3CN)_2$,[9e] 0.279 and 0.289 Å in $Ni_3(dpa)_4(AnCOO)_2$.[9h] For the oxidized species containing Ni_3^{7+} cores, the *d* distances are 0.102 Å for $[Ni_3(dpa)_4](PF_6)_3$,[16] and 0.103 Å for $[Ni_3(depa)_4](PF_6)_3$.[9e] These data show a strong correlation between the value of *d* and how strongly bound is the group in the axial position with those groups such as acetonitrile, chloride and carboxylates having *d* values of 0.23–0.29 Å while those with the weaker donor PF_6 in the range of about 0.1 Å.

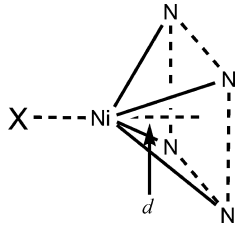


Figure 2. A drawing showing the environment of the outer units in **1** with a square base of four nitrogen atoms and the out of plane nickel atom; *d* is the distance from the Ni atom to the center of the idealized square base. The axial ligand is represented as X.

It should be noted that the distance that the outer Ni atoms are pulled from the square plane has important implications in the Ni···Ni separations in these trinickel complexes. Because the central units are typically square planar, the further away from the plane the outer Ni atoms are, the longer the Ni···Ni separation would be expected, and this is clearly seen from the data in Table 2.

In view of these results it is useful to make a comparison of the separation between nickel atoms in the species with Ni_3^{6+} and Ni_3^{7+} cores. As mentioned earlier there are two compounds with an oxidized core, $[Ni_3(dpa)_4](PF_6)_3$[16] and $[Ni_3(depa)_4](PF_6)_3$.[9e] Each has F atoms from PF_6 groups about 2.42–2.45 Å away from the outer Ni atoms. This separation is about 0.25 Å closer than that in **1**, which was assumed to be consistent with the increase in the positive charge of the trinickel unit. Interestingly there is not a significant difference in the distance *d* between the oxidized species and **1**. These results again suggest that the hexafluorophosphate anions have little influence in the electronic environment of the outer units. However, it raises an important issue as to whether the shortening in the Ni···Ni separations in the oxidized species relative to those in the unoxidized species with strongly coordinated groups is due to bond formation as had been suggested,[9,16] or whether this is simply due to the change in coordination of the outer

units. If the Ni···Ni separations in **1** are adjusted, assuming that the axial Cl atom could be replaced by a second PF_6, these separations would be expected to be very similar to those in the oxidized species.

Although this issue cannot be answered unambiguously by the present data, the increased charge in the oxidized Ni_3^{7+} units would be expected to lead to an increase in the separation between nickel atoms as is known for the oxidation of $Cu_3(dpa)_4Cl_2$ to $[Cu_3(dpa)_4Cl_2]SbCl_6$.[16] However, upon oxidation of a Ni_3^{6+} to a Ni_3^{7+} core removal of a non-bonding electron would be expected to favor bond formation. It appears the effect of these forces essentially cancels out and the observed distances and those adjusted by the changes in coordination are quite similar. This type of cancellation has been observed frequently in dinuclear paddlewheel compounds.[19] It should also be noted that there is now strong additional evidence for the existence of Ni–Ni bonding in cations of the type $[Ni_2(formamidinate)_4^+]$[20] and in large EMACs such as those containing five nickel atoms.[21]

Magnetism

The variable-temperature magnetic data are shown in Figure 3. The shape of the curves is very different from those resulting from symmetrical Ni_3^{6+} EMACs.[7,12] Studies on a series of symmetrical trinickel compounds have shown that the χT values are less than 2.00 emu K/mol for two independent $S = 1$ centers, which suggests that the spins are partially randomized at high temperature.[7,12] Each of the two terminal Ni atoms contribute two unpaired electrons while the central Ni atom does not supply unpaired electrons (Scheme 3, a) because of its d^8 square-planar unit that resembles the $Ni(CN)_4^{2-}$ anion.[22] The χT values decrease as the temperature decreases, and χT values are essentially zero below 50 K because of antiferromagnetic coupling.

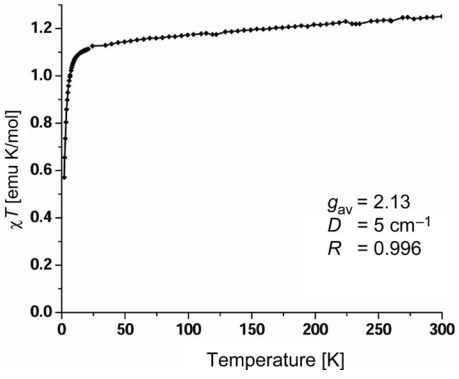
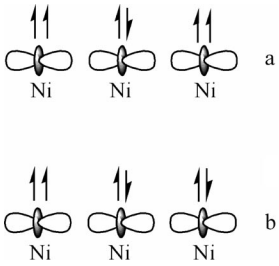


Figure 3. Magnetic susceptibility data for **1** in the range of 2 to 300 K. See text for details on the fitting.

However, in **1** the χT values are about 1.20 emu K/mol at room temperature, and do not significantly decrease as the temperature decreases to ca. 25 K. The magnetic data strongly suggest that the small pull from the square-planar plane of the Ni atom in the vicinity of the PF_6 anion does not have important consequences to the magnetism above 25 K, and this unit can be considered as behaving as a square-planar species. Thus **1** is unusual among the family of Ni_3 EMACs in that it has Curie-like magnetism; that is, the magnetic behavior observed arises from an $S = 1$ state of the pyramidal nickel atom coordinated by the acetonitrile ligand, represented in Scheme 3, b. Under this description, the magnetic data was fit using the Equation (1)



Scheme 3. The electrons in an EMAC with a) two terminal five-coordinate units and b) with only one such unit.

$$\chi = \frac{N\beta^2 g^2}{kT} \cdot \frac{\left(e^{-D/kT} + \left(\frac{2kT}{D}\right)\left(1 - e^{-D/kT}\right)\right)}{\left(1 + 2e^{-D/kT}\right)} \quad (1)$$

where D is the ZFS parameter, k is the Boltzmann constant, N is Avogadro's number, and β is the Bohr magneton. The fitting was done for the temperature range of 2–20 K to minimize the interference from temperature-independent paramagnetism, likely due to a small amount of paramagnetic impurity. Under these conditions, g_{av} is 2.13 and $D = -5$ cm^{-1}. The latter is responsible for the drop in χT below 25 K.

Concluding Remarks

The present study shows that an unsymmetrical Ni_3^{6+} EMAC having only one strongly bound axial ligand can be synthesized in good yield. The electronic spectrum and magnetic properties of this Ni_3^{6+} chain which has a weakly bound axial ligand is greatly changed relative to those having two strongly bound axial ligands. One terminal Ni atom in **1** is paramagnetic with two unpaired electrons due to the square-pyramidal coordination, while the other terminal Ni atom and the central Ni atom are diamagnetic and nearly square planar. This shows that magnetic behavior in this type of EMACs can be tuned by the electron donor ability of the axial ligands.

Experimental Section

Materials and Methods: All reactions and manipulations were carried out under dry nitrogen using standard Schlenk techniques. Solvents were either distilled from appropriate drying agents under nitrogen or purified using a Glass Contour solvent system. Chemicals were purchased from Aldrich. Anhydrous nickel chloride and silver(I) hexafluorophosphate were dried overnight under vacuum

at 70 °C and 2,2′-dipyridylamine was sublimed prior to use. The symmetrical starting material $[Ni_3(dpa)_4(CH_3CN)_2](PF_6)_2$ was prepared as reported.[9e]

Physical and Characterization Measurements: Elemental analysis was performed by Robertson Microlit Laboratories, Madison, NJ on crystalline samples that had been dried under vacuum. Mass spectrometric data were recorded at the Laboratory for Biological Mass Spectrometry at Texas A&M University. The UV/Vis spectrum was measured with a Shimadzu UV-2501PC spectrophotometer in dichloromethane solution. Variable temperature magnetic susceptibility measurements were performed with a Quantum Design SQUID magnetometer MPMS-XL from 2 to 300 K using crushed crystalline samples.

Preparation of $[Ni_3(dpa)_4(CH_3CN)](PF_6)_2·2CH_2Cl_2$ ($1·2CH_2Cl_2$): Dichloromethane (15 mL) was added to a flask containing a crystalline sample of purple $[Ni_3(dpa)_4(CH_3CN)_2](PF_6)_2$ (120 mg, 0.100 mmol). The resulting purple solution was stirred overnight, and the solvent was then removed at ambient temperature under vacuum. The remaining deep purplish-red solid was washed with hexanes (2 × 15 mL) and ether (2 × 15 mL), and then dissolved in CH_2Cl_2 (10 mL). A layer of hexanes (30 mL) was added on top of the solution. Deep purplish-red crystals formed within a week. Yield 92 mg, 68%. $C_{42.5}H_{36}ClF_{12}N_{13}Ni_3P_2$ (**1**·0.5CH_2Cl_2): calcd. C 41.50, H 2.95, N 14.80; found C 41.96, H 2.71, N 14.86. Mass spectrum, ESI$^+$: m/z = 428.05 for $[Ni_3(dpa)_4]^{2+}$. UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 450 (750), 520 nm (3000).

X-ray Structural Determination: A suitable crystal was mounted at the end of a quartz fiber with the aid of a small amount of Paratone-N oil and then placed on a goniometer's head. X-ray diffraction data for **1**·2CH_2Cl_2 were collected at 213 K with a Bruker SMART 1000 CCD area detector system.[23] Data reduction and integration were performed using the software SAINTPLUS.[24] Absorption corrections were applied using the program SADABS.[25] The structure was solved by direct methods and refined using the SHELXL-97 program.[26] Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were added at calculated positions based on a riding model. Non-hydrogen atoms, except some disordered atoms, were refined with anisotropic displacement parameters. Crystallographic data for **1**·2CH_2Cl_2 are given in Table 3.

Table 3. Crystallographic data for **1**·2CH_2Cl_2.

	1·2CH_2Cl_2
Empirical formula	$C_{44}H_{39}Cl_4F_{12}N_{13}Ni_3P_2$
M_r	1357.75
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	16.152(5)
b [Å]	19.595(6)
c [Å]	19.984(6)
α [°]	96.656(5)
β [°]	111.920(5)
γ [°]	107.988(5)
V [Å^3]	5386(3)
Z	4
T [K]	213
λ [Å]	0.71073
$d_{calcd.}$ [g cm^{-3}]	1.674
F (000)	2736
Crystal size [mm]	0.22 × 0.21 × 0.11
Reflections collected	47772
Independent reflections	19666
Parameters	1382
R_{int}	0.0317
Completeness	98.4%
Goodness-of-fit on F^2	1.016
R_1,[a] wR_2[b] ($I > 2\sigma I$)	0.0687, 0.1912
R_1,[a] wR_2[b] (all data)	0.1091, 0.2356

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

CCDC-654608 (for **1**·2CH_2Cl_2) contains 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.

Acknowledgments

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