Syntheses of Square-planar Nickel-(II) and -(I) Complexes of an Octaaza Macrohexacyclic Ligand and Crystal Structure of the Nickel(II) Complex†

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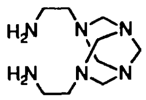
The square-planar nickel(II) complex of the octaaza macrohexacyclic ligand 1,3,6,8,10,12,15,17-octaazahexacyclo[15.6.1.1^{3,17}.1^{6,0}.1^{8,12}.0^{18,23}]heptacosane, [NiL^4][PF$_6$]$_2$, has been synthesized by template condensation of the nickel(II) complex of 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo-[3.3.1]nonane with formaldehyde and *trans*-cyclohexane-1,2-diamine. The complex exhibits an unusually strong ligand-field strength compared with other square-planar nickel(II) complexes of 14-membered azamacrocycles. Cyclic voltammetry indicated a one-electron reduction potential at −1.32 V *vs.* Ag–AgCl and no oxidation peak up to +1.59 V. The complex crystallizes in the orthorhombic space group $Pna2_1$, with a = 17.934(2), b = 16.056(3), c = 9.612(1) Å and Z = 4. The structure was solved by the heavy-atom method and refined by full-matrix least squares to a final R = 0.0447 for 2092 observed [$I > 2\sigma(I)$] reflections. The ligand contains bicyclononane and tricyclotetradecane cage ring moieties fused at both ends of two ethylenediamine groups. The average Ni–N distance is 1.904(7) Å. The N–N bite distances are 2.706(6) and 2.698(6) Å for the five-membered chelate rings and 2.703(6) and 2.665(6) Å for the six-membered chelate rings so that the cavity size of the ligand is similar to that of 1,4,7,10-tetraazacyclododecane. Reduction of [NiL^4][PF$_6$]$_2$ with Na/Hg gave [NiL^4]PF$_6$, which shows an anisotropic axial EPR powder spectrum with g values of $g_{\parallel} > g_{\perp}$.

Properties of macrocyclic complexes such as ligand-field strength and electrochemical redox potentials depend on the ring size, substituents, ligand unsaturation and size of any fused rings.[1–5] In particular the presence of tertiary amine donors in a macrocyclic ligand alters such properties.[6–10] For example, N-alkylation of secondary nitrogens in nickel(II) complexes of tetraaza macrocyclic ligands results in a decrease in the ligand-field strength and an anodic shift in both the oxidation and reduction potentials. It has been suggested that these changes are associated with the longer Ni–N bond distances observed for the N-alkylated complexes. However, there have been only a limited number of reports on the crystal structures of macrocyclic complexes containing exclusively tertiary nitrogen donors, and the lengthening of Ni–N bond distances involving tertiary nitrogen donors has not been fully proven. In addition, Ni–N distances involving tertiary amines are not always longer than those involving secondary amines in macrocyclic complexes which contain both secondary and tertiary nitrogen donors.[5,11]

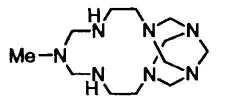
We have prepared the nickel(II) complex of the macrohexacyclic ligand 1,3,6,8,10,12,15,17-octaazahexacyclo[15.6.1.1^{3,17}.1^{6,10}.1^{8,12}.0^{18,23}]heptacosane (L^4), which contains tertiary nitrogen donors exclusively. Contrary to nickel(II) complexes of N-alkylated macrocyclic ligands, the complex of L^4 shows an unusually strong ligand-field strength and short Ni–N bond distances. This paper therefore describes the synthesis, properties, and crystal structure of [NiL^4][PF$_6$]$_2$.

Results and Discussion

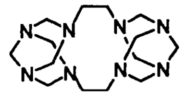
Synthesis and Properties.—Previously, we synthesized the nickel(II) complexes of L^1 and L^2 by template condensation of an amine and formaldehyde as given by equations (1) and (2).[11]



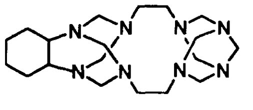
L^1



L^2



L^3



L^4

$$\mathrm{Ni^{2+} + H_2NCH_2CH_2NH_2 + CH_2O + NH_4OH \xrightarrow{MeOH\text{–}H_2O\,(1:1)} [NiL^1]^{2+}} \quad (1)$$

$$\mathrm{[NiL^1]^{2+} + CH_2O + NH_2Me \xrightarrow{MeOH} [NiL^1]^{2+}} \quad (2)$$

We attempted to prepare the nickel(II) complex of L^3, which contains two symmetric cage ring moieties, but the synthesis was never successful [equation (3)]. However, the new octaaza

$$\mathrm{[NiL^1]^{2+} + CH_2O + NH_4OH \overset{MeOH}{\not\longrightarrow} [NiL^3]^{2+}} \quad (3)$$

macrohexacyclic complex [NiL^4][X]$_2$ (X = BPh$_4$ or PF$_6$) can be prepared from the template condensation of [NiL^1]$^{2+}$, formaldehyde and *trans*-cyclohexane-1,2-diamine, followed by the addition of a salt of the appropriate anion [equation (4)].

$$\mathrm{[NiL^1]^{2+} + CH_2O + C_6H_{10}(NH_2)_2\text{-}1,2 \xrightarrow{MeOH} [NiL^4]^{2+}} \quad (4)$$

In the reaction, formaldehyde links two amine moieties from ethylenediamine and *trans*-cyclohexane-1,2-diamine to give methylenediamine (NCH$_2$N) linkages. It has been demonstrated

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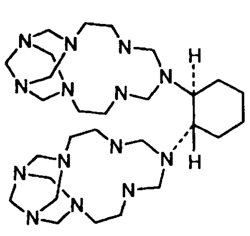
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

that the methylenediamine linkage is unstable unless both of the nitrogen atoms are tertiary,[12] and that secondary nitrogen atoms in such a linkage should be stabilized by co-ordination to metal ions.[4,5,11,13,14] In the present macrocycle L^4, all the nitrogen atoms involving the methylenediamine linkages are tertiary. The reaction might produce the dinickel(II) complex of the bis-macrocyclic ligand L^5 also, but we were able to isolate only the nickel(II) complex of L^4. The ligand L^4 is unique in that it contains tertiary nitrogen atoms exclusively and acts as a tetradentate ligand to form a square-planar nickel(II) complex. The complex consists of a 14-membered hexaaza macrocyclic framework to which two additional triaza six-membered chelate rings are fused to each nitrogen atom of the ethylenediamine moieties.

The IR spectrum of $[NiL^4]^{2+}$ shows no N–H stretch, confirming that all the nitrogens are tertiary and the complex is diamagnetic, indicating a square-planar d^8 electronic structure. The ^{13}C NMR spectrum shows 10 unique carbon peaks, consistent with the ligand structure. The spectral and electrochemical data of the complex are summarized in Table 1, together with those of other nickel(II) macrocyclic complexes for comparison. The electronic absorption spectrum of $[NiL^4][PF_6]_2$ shows λ_{max} at 425 nm (ε 209 $dm^3\ mol^{-1}\ cm^{-1}$) in MeCN, a wavelength *ca.* 30 nm shorter than those of other 14-membered macrocyclic nickel(II) complexes of square-planar geometry,[14] and shorter even than that of $[NiL^6]^{2+}$ (L^6 = 8,10-dimethyl-1,4,7,11-tetraazacyclotridecane).[15] These indicate that $[NiL^4]^{2+}$ shows an extraordinarily strong ligand-field strength contrary to nickel(II) macrocyclic complexes with tertiary nitrogen donors such as 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane which exhibit much weaker ligand-field strengths than those with secondary nitrogen donors such as cyclam (1,4,8,11-tetraazacyclotetradecane). The strong ligand-field strength of $[NiL^4]^{2+}$ may be attributed to the constriction effect of L^4 towards the nickel ion as a result of the abnormally short N–N bite distances of the cage ring moieties, as shown in the crystal structure of the complex.

Cyclic voltammetry shows a reversible one-electron reduction potential at -1.32 V *vs.* Ag–AgCl, which is similar to the -1.33 V observed for $[NiL^2]^{2+}$. However, $[NiL^4]^{2+}$ is not oxidized up to $+1.59$ V while $[NiL^2]^{2+}$ is oxidized at $+1.38$ V. The difficulty in oxidizing the complex may be attributed to the inflexibility of L^4 and the small hole size, as shown in the crystal structure, which cannot accommodate a Ni^{III} ion in an octahedral geometry. Usually, Ni^{III} species form octahedral complexes with two axial ligands and average Ni^{III}–N bond distances of 1.94–1.98 Å.[16,17]



L^5

Previously, we reported the syntheses and crystal structures of various nickel(I) macrocyclic complexes including that of L^2.[18] The similar reduction potentials of $[NiL^4]^{2+}$ and $[NiL^2]^{2+}$ imply that L^4 is also able to stabilize the Ni^I state. In fact, the nickel(I) complex of L^4 has been obtained by reducing $[NiL^4]^{2+}$ with Na/Hg in MeCN under the strict exclusion of air; $[NiL^4]^+$ is extremely sensitive to oxygen and moisture. The spectroscopic properties of $[NiL^4]PF_6$ are summarized in Table 2, together with those of $[NiL^2]ClO_4$ for comparison. The λ_{max} value for $[NiL^4]^+$ is *ca.* 120 nm higher than that of the corresponding Ni^{II} complex. The EPR spectrum of $[NiL^4]PF_6$ is shown in Fig. 1; the anisotropic axial *g* values ($g_{\parallel} > g_{\perp}$) indicate the square-planar d^9 electronic structure.[18,19]

All the Ni^I macrocyclic complexes whose crystal structures have been reported so far have shown two different sets of Ni–N bond distances rather than a simple expansion of the macrocyclic hole.[18,20] This is consistent with the EXAFS (extended X-ray absorption fine structure) results of Ni^I F430.[21] However, these Ni^I macrocyclic complexes contain two different types of nitrogen donors such as tertiary and secondary nitrogens or amine and imine nitrogens. Therefore, in order to generalize the occurrence of two different sets of Ni–N bond distances, it is necessary to obtain the crystal structure of a nickel(I) complex containing nitrogen donors in the same environment. We are currently attempting to obtain single crystals of $[NiL^4]PF_6$ to determine its structure.

Crystal Structure of $[NiL^4][PF_6]_2$.—A view of the $[NiL^4]^{2+}$ cation with the atom numbering scheme is shown in Fig. 2. The final atomic coordinates are listed in Table 3 and selected bond distances and angles in Table 4. The four donor nitrogen atoms of L^4 form a square-planar co-ordination plane approximately parallel to the *ab* plane with a maximum deviation of 0.002 Å. The nickel ion is displaced by 0.057 Å from the least-squares plane, showing a slight square-pyramidal distortion. The average Ni–N distance is 1.904(7) Å, which falls in the range (1.86–1.94 Å) normally observed for square-planar nickel(II) complexes of tetraazamacrocycles.[22–24] However, it is 0.015 Å shorter than that observed in $[NiL^2][ClO_4]_2$.[11] The extraordinarily strong ligand-field strength of $[NiL^4]^{2+}$ must be attributed to the short Ni–N bond distances.

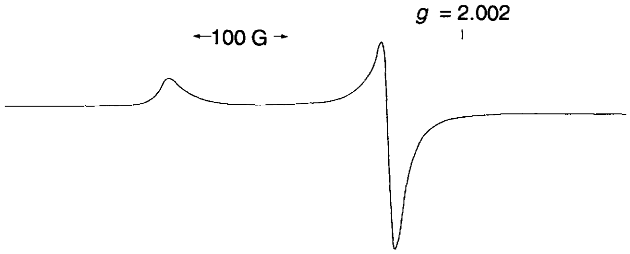


Fig. 1 EPR powder spectrum of $[Ni^IL^4]PF_6$ measured at room temperature

Table 1 Spectroscopic and electrochemical data for nickel(II) macrocyclic complexes

	$\lambda_{max}{}^a$/nm (ε/$dm^3\ mol^{-1}\ cm^{-1}$)	$E_{ox}{}^{b,c}$/V Ni^{II}–Ni^{III}	$E_{red}{}^{b,c}$/V Ni^{II}–Ni^I	Ref.
$[NiL^4][PF_6]_2$	425 (209), 202 (188 000)	> +1.59	−1.32 (r)	This work
$[NiL^2][ClO_4]_2$	442 (80), 438 (83)^d	+1.38 (r)	−1.33 (r)	11
$[Ni([14]aneN_4)][ClO_4]_2$	455^d	+0.97 (r)	−1.40 (r)	1, 6
$[Ni([13]aneN_4)]^{2+}$		$+1.0 \longrightarrow 1.2$ (i)	−1.40 (r)	1
$[NiL^6][PF_6]_2{}^e$	428 (145)^f			15

^{a} Measured in MeCN unless otherwise indicated. ^{b} Measured in MeCN with 0.1 mol dm^{-3} NBu_4PF_6; reference electrode Ag–AgCl. ^{c} i = Irreversible; r = reversible. ^{d} Measured in $MeNO_2$. ^{e} L^6 = 8,10-dimethyl-1,4,7,11-tetraazacyclotridecane. ^{f} Measured in H_2O.

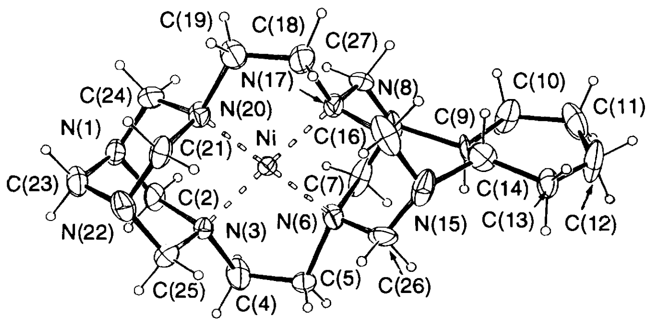


Fig. 2 An ORTEP view of the cation in [NiL^4][PF$_6$]$_2$ with the atom numbering scheme used. Thermal ellipsoids are drawn at the 25% probability level. Only the major sites of C(9) and C(14) are shown

Table 2 Spectroscopic data for nickel(I) complexes

		EPR[b]	
	λ_{max}[a]/nm (ε/dm^3 mol^{-1} cm^{-1})	$g_\parallel$	$g_\perp$
[NiL^4]PF$_6$	549 (170), 323 (1800)	2.200	2.050
[NiL^2]ClO$_4$[c]	538 (600), 330 (2020)	2.240	2.062

[a] Measured in MeCN. [b] The spectra were measured with powder samples at room temperature. [c] Ref. 18.

In the five-membered chelate rings the N(3)–N(6) and N(17)–N(20) bite distances are 2.706(6) and 2.698(6) Å respectively and the bite angles 90.4(2) and 90.3(2)°. In the six-membered chelate rings the N(3)–N(20) and N(6)–N(17) bite distances are 2.703(6) and 2.665(6) Å respectively and the bite angles 90.3(2) and 88.8(2)°. These indicate that N–N bite distances involving the cage ring moieties are similar to those of the five-membered chelate rings although each cage ring consists of two six-membered chelate rings. Therefore, the complex of L^4 is more similar to the complex of 1,4,7,10-tetraazacyclododecane ([12]aneN$_4$), which consists of four five-membered chelate rings, rather than that of 1,4,8,11-tetraazacyclotetradecane ([14]aneN$_4$). It was reported that [12]aneN$_4$ itself could not encompass a Ni^{II} ion in a square-planar arrangement and formed only high-spin five- and six-co-ordinate complexes in a *cis*-folded arrangement.[25–27]

There are pseudo-symmetric relationships between the atoms in the cation. The portion containing the bicyclononane and ethylenediamine moieties has a pseudo-mirror symmetry passing through the nickel ion and C(23) at the apex of the bicyclononane ring and perpendicular to the co-ordination plane. The disordered cyclohexyl moieties have pseudo-two-fold rotational symmetry and assume a somewhat flattened half-chain conformation. All of the four six-membered chelate rings and the two seven-membered rings fused to the cyclohexyl ring assume a stable chair conformation. The ethylenediamine moieties assume a gauche conformation.

Table 3 Atomic coordinates* (× 10^4) for [NiL^4][PF$_6$]$_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	2124(1)	253(1)	−298	C(23)	3287(3)	2262(4)	−248(21)
N(1)	3029(6)	1830(7)	−1517(12)	C(24)	3366(8)	993(9)	−1521(16)
C(2)	2240(7)	1832(9)	−1561(15)	C(25)	2210(6)	1825(10)	960(14)
N(3)	1894(2)	1416(3)	−254(14)	C(26)	905(7)	−473(9)	993(15)
C(4)	1074(4)	1482(4)	−419(27)	C(27)	2034(8)	−1301(9)	−1566(19)
C(5)	699(4)	789(4)	218(10)	P(1)	896(1)	4119(1)	−276(5)
N(6)	1091(2)	−11(3)	−237(16)	F(1A)	357(6)	3356(5)	−605(14)
C(7)	923(7)	−509(10)	−1606(12)	F(1B)	528(8)	4622(8)	−1516(12)
N(8)	1273(7)	−1305(6)	−1683(11)	F(1C)	1410(6)	4887(6)	84(17)
C(9)	726(25)	−1917(14)	−857(28)	F(1D)	1243(7)	3600(8)	969(13)
C(9′)	1052(20)	−2086(26)	−1027(37)	F(1E)	284(5)	4485(8)	756(12)
C(10)	504(8)	−2608(9)	−1726(14)	F(1F)	1506(7)	3753(9)	−1290(15)
C(11)	144(11)	−3312(10)	−1054(22)	F(1A′)	521(9)	3411(7)	642(14)
C(12)	50(11)	−3202(10)	442(18)	F(1B′)	107(4)	4376(10)	− 861(18)
C(13)	456(5)	−2566(7)	1376(15)	F(1C′)	1280(7)	4808(7)	−1203(13)
C(14)	943(22)	−2073(22)	543(29)	F(1D′)	1692(5)	3841(11)	291(19)
C(14′)	677(22)	−1779(26)	375(29)	F(1E′)	818(11)	4755(7)	965(12)
N(15)	1213(8)	−1265(8)	1145(11)	F(1F′)	985(9)	3462(7)	−1507(12)
C(16)	2022(10)	−1278(9)	1062(14)	P(2)	3407(1)	5738(1)	−276(4)
N(17)	2340(2)	−908(3)	−226(20)	F(2A)	2903(2)	6546(2)	−268(10)
C(18)	3160(4)	−965(5)	253(12)	F(2B)	2909(3)	5346(4)	−1467(6)
C(19)	3564(3)	−306(4)	−128(31)	F(2C)	3914(3)	4925(3)	−282(10)
N(20)	3158(2)	502(3)	−236(16)	F(2D)	3927(3)	6130(5)	893(6)
C(21)	3345(7)	1017(9)	1035(14)	F(2E)	3925(3)	6133(4)	−1445(6)
N(22)	3026(7)	1825(8)	976(12)	F(2F)	2902(3)	5341(4)	900(7)

* Site occupancy factors are 0.6371 for C(9) and C(14), 0.3629 for C(9′) and C(14′), 0.5074 for F(1A)–F(1F) and 0.4926 for F(1A′)–F(1F′).

Table 4 Selected bond lengths (Å) and angles (°) for [NiL^4][PF$_6$]$_2$

Ni–N(20)	1.897(4)	Ni–N(6)	1.900(5)
Ni–N(17)	1.906(5)	Ni–N(3)	1.912(4)
C–N	1.37(2)–1.60(3) (av. 1.48 ± 0.05)	C–C	1.33(1)–1.64(4) (av. 1.47 ± 0.08)
P–F	1.576(5)–1.593(5) (av. 1.585 ± 0.006)		
N(20)–Ni–N(6)	176.3(7)	N(20)–Ni–N(17)	90.3(2)
N(6)–Ni–N(17)	88.8(2)	N(20)–Ni–N(3)	90.3(2)
N(6)–Ni–N(3)	90.4(2)	N(17)–Ni–N(3)	176.6(7)

Experimental

Materials.—All chemicals and solvents used in the syntheses were of reagent grade and used without further purification. However, they were purified according to the literature[28] for the physicochemical measurements. The complex $[NiL^1][ClO_4]_2$ was prepared by the template condensation reaction of ethylenediamine, formaldehyde and ammonia in the presence of Ni^{II} ion as previously described in the literature.[11]

Measurements.—Infrared spectra were recorded on Perkin-Elmer 782 spectrophotometer, ^{13}C NMR spectra on a Bruker AC 80 FT NMR spectrometer and electronic absorption spectra on a Shimadzu 260 UV/VIS spectrophotometer. Cyclic voltammetry was carried out with a BAS 100A Electrochemical analyser and Ametek DMP-40 series digital plotter. The electrochemical data were obtained in MeCN with 0.1 mol dm^{-3} NBu_4PF_6. The working electrode was a platinum disc, the auxiliary electrode a platinum wire and the reference electrode Ag–AgCl. Elemental analyses were performed by the Korea Basic Science Center, Seoul.

Synthesis of (1,3,6,8,15,17,20,22-*Octaazahexacyclo*[20.1.$1^{1,20}.1^{3,22}.1^{6,15}.1^{8,17}.0^{9,14}$]*heptacosane)nickel*(II) *Hexafluorophosphate*, $[NiL^4][PF_6]_2$.—**CAUTION**: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of materials should be prepared, and these should be handled with great care. The complex $[NiL^1][ClO_4]_2$ (2.0 g) was dissolved in water–MeOH (1 : 1, 60 cm^3) and 36% aqueous formaldehyde (2.0 cm^3) and *trans*-cyclohexane-1,2-diamine (2.0 cm^3) were added. The mixture was heated at reflux for 24 h until a yellow solution resulted. The solution was filtered whilst hot to remove any insoluble material and a saturated MeOH solution of $LiClO_4$ (2 g) was added. The solution was allowed to stand at room temperature until a yellow precipitate of $[NiL^4][ClO_4]_2$ formed which was filtered off, washed with methanol and dried *in vacuo*. The precipitate was purified by exchanging the anions as follows. Crude $[NiL^4][ClO_4]_2$ (1 g) was dissolved in MeCN (5 cm^3) and $NaBPh_4$ (3 g) was added. The solution was centrifuged and filtered to remove insoluble material. Diethyl ether was added dropwise and the solution allowed to stand for 2 d, during which time needle shaped crystals of $[NiL^4][BPh_4]_2$ formed. The crystals were filtered off and washed with MeCN–Et_2O (1 : 1). Yield: *ca*. 60%. Molar conductance 266 Ω^{-1} dm^3 mol^{-1} cm^{-1}.

Single crystals of $[NiL^4][PF_6]_2$ for the crystal structure analysis were obtained by dissolving $[NiL^4][BPh_4]_2$ in MeCN and adding NH_4PF_6 (3g). The resulting white precipitate of NH_4BPh_4 was filtered off to obtain a clear yellow solution. To the solution was added Et_2O dropwise to induce crystallization. The crystals were filtered off, washed with MeCN–Et_2O (1 : 1) and dried *in vacuo* (Found: C, 31.85; H, 5.20; N, 15.25. Calc. for $C_{19}H_{36}F_{12}N_8NiP_2$: C, 31.35; H, 5.00; N, 15.45%); ^{13}C NMR (80 MHz; solvent CD_3CN): δ, 25.2, 32.0, 51.3, 53.3, 67.8, 68.5, 70.2, 73.9, 74.2, 77.0.

Synthesis of (1,3,6,8,15,17,20,22-*Octaazahexacyclo*[20.1.$1^{1,20}.1^{3,22}.1^{6,15}.1^{8,17}.0^{9,14}$]*heptacosane)nickel*(I) *Hexafluorophosphate*, $[NiL^4]PF_6$.—The complex $[NiL^4][PF_6]_2$ (0.7 g) and Na/Hg (10% Na, 5 g) were stirred in dry, degassed MeCN (20 cm^3) for 30 min under a nitrogen atmosphere. The solution turned deep violet, which was filtered and then concentrated to *ca*. one quarter by volume under vacuum. The solution was allowed to stand in a refrigerator for 2 d during which time violet crystals formed which were filtered off, washed with degassed MeCN and dried *in vacuo*.

Structure Determination of $[NiL^4][PF_6]_2$.—*Crystal data*. $C_{19}H_{36}F_{12}N_8NiP_2$, $M = 725.17$, orthorhombic, space group $Pna2_1$ (no. 33), $a = 17.934(2)$, $b = 16.056(3)$, $c = 9.612(1)$ Å, $U = 2767.8(7)$ Å^3, $Z = 4$, $D_c = 1.740$ g cm^{-3}, $F(000) = 1488$. Crystal size: *ca*, 0.6 × 0.5 × 0.4 mm, μ(Mo-Kα) = 9.20 cm^{-1}.

Data collection and processing. Enraf–Nonius CAD4 diffractometer, ω–2θ mode with ω scan width = 1.0 + 0.35 tan θ, ω scan speed 2–7° min^{-1}, zirconium-filtered graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å); 2584 independent reflections (*h* 0–21, *k* 0–19, *l* 0–11) measured ($3 < 2\theta < 50°$), 2092 (81.0%) observed with $I > 2\sigma(I)$. Crystal quality judged to be poor from the ω scans of several intense reflections which showed the width at half-height of 0.80° at a take-off angle of 2.8°. No noticeable intensity change during the data collection. No absorption and extinction corrections made.

Structure analysis and refinement. The structure was solved by heavy-atom methods with SHELXS 86[29] and refined by full-matrix least-squares methods on F^2 with SHELXL 93[30] in a painstaking procedure due to the presence of disorder and pseudo symmetry. Systematic absences were consistent with either non-centrosymmetric space group $Pna2_1$ (no. 33) or centrosymmetric *Pnma* (no. 62; when *k* and *l* are interchanged) and initial structure was solved in both space groups. However, in the centrosymmetric space group *Pnma* in which both the ligand and the anions should possess crystallographic *mm* symmetry, many problems in model building and refinement could not be resolved. First, the fluorine atoms in the disordered PF_6 anion which were identified in the difference map and could be refined, violated the *mm* symmetry. Secondly, the bridging C(9) and C(14) atoms in the fused cyclohexyl moiety should be disordered about the mirror plane that is perpendicular to the co-ordination plane. Otherwise, the cyclohexane ring becomes flat and the two carbon atoms cannot have the sp^3 configuration. However, the initial disorder model was not stable in the refinement process with the two atoms shifting to the mirror plane. Finally the carbon atoms of the two ethylenediamine moieties in the difference map were not found in the co-ordination mirror plane, suggesting a disorder about this mirror plane, but the disorder model was not stable during the refinement either.

The best result was obtained in the non-centrosymmetric space group $Pna2_1$ with a model that contained a disordered PF_6 anion and disordered atom pairs of C(9) and C(14). Among various models tested this one with two sets of bridging carbon atoms, which are approximately related by mirror symmetry, was the chemically most reasonable for the fused cyclohexyl moiety and gave the lowest *R* value. Other carbon atoms in the cyclohexane ring could not be resolved into disordered sites. The two PF_6 anions were refined anisotropically with restraints of idealized octahedral geometry (P–F 1.587 Å) assuming a rotational disorder for one PF_6. The site occupancy factor for the major sites of C(9) and C(14) was refined to 0.64(6). All hydrogen atoms were included in the refinement using the AFIX option of SHELXL 93 with the isotropic thermal parameters fixed with values of 1.2 times those of the bonded atoms. No constraints or restraints were applied to the cation. High correlation between the atom pairs related by the pseudo mirror in the co-ordination plane was observed. Final $R = 0.0447$ for 2092 observed reflections [$I > 2\sigma(I)$] and 0.0662 for all 2584 reflections; 452 parameters and 87 restraints; goodness-of-fit on $F^2 = 0.999$; largest difference peak and hole were 0.411 and -0.357 e Å^{-3}, respectively. Atomic scattering factors and the terms of anomalous dispersion correction were as incorporated in SHELXL 93. Fig. 2 was drawn using ORTEP.[31]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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