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Synthesis and Characterization of the Macrocyclic Complexes

$[\text{Ni}(\text{Me}_2[14]\text{dienatoN}_2\text{P}_2)]\text{PF}_6$ and $[\text{Ni}(\text{Me}_2[16]\text{dieneN}_2\text{P}_2)](\text{PF}_6)_2$. Crystal Structure of $[\text{Ni}(\text{Me}_2[16]\text{dieneN}_2\text{P}_2)](\text{PF}_6)_2 \cdot 0.5\text{H}_2\text{O}$

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The titled macrocyclic complexes were synthesized by acid-catalyzed rearrangement of sexidentate phosphine amino Schiff base Ni(II) complexes prepared from 1 equiv of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and bis(acetylacetonate) trimethylenebis[(3-amino-propyl)phenylphosphine] or bis(acetylacetonate) trimethylenebis[(2-aminoethyl)phenylphosphine]. Ring closure was accomplished in a mixture of water and acetic acid at pH 4 and results in the elimination of 1 equiv of Hacac. Infrared, visible spectra, and magnetic susceptibility measurements indicate that the complexes contain square-planar, diamagnetic Ni(II) bonded to a macrocyclic diphosphine-diimine ligand. Proton and $^{31}\text{P}\{^1\text{H}\}$ NMR data suggest that the products are isomerically pure in either the meso or the racemic forms. The meso structure has been confirmed by single-crystal X-ray diffraction analysis of the 16-membered ring diene complex. This complex crystallizes in the monoclinic space group $P2_1/c$, with $a = 14.049$ (12) Å, $b = 12.367$ (8) Å, $c = 20.129$ (9) Å, and $\beta = 105.11$ (5)° at $T = 20$ (1) °C, $\lambda = 0.71069$ Å (Mo K α radiation), and $Z = 4$. Least-squares refinement on F using 2230 unique reflections yielded a conventional R factor of 0.076. The two phosphorus and the two nitrogen atoms form a well-defined plane with the nickel atom lying 0.07 Å out of the plane (Ni—P = 2.182 (3) and 2.188 (4) Å; Ni—N = 1.916 (9) and 1.918 (8) Å; C=N = 1.29 (2) Å). The diimine ring exists in the boat conformation with the N=C bonds orientated at a 46° angle with respect to the N_2P_2 plane.

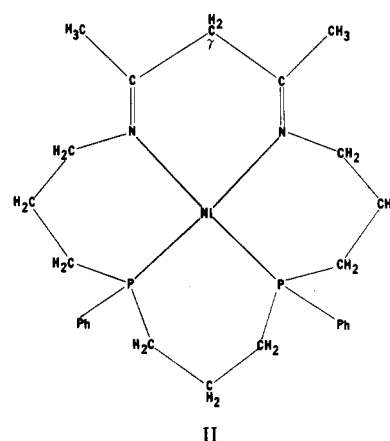
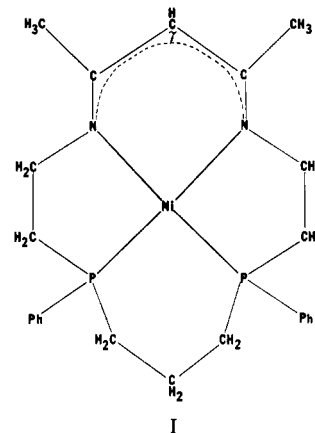
Introduction

There are numerous examples of macrocyclic metal complexes in which the macrocyclic ligand contains heteroatoms.^{2,3} Very few of these reported complexes, however, have phosphorus and nitrogen donor combinations. In fact, there are only two reports where this is the case. Meek and Riker-Nappier have published on four- and five-coordinate nickel(II) complexes containing N_3P tetradentate macrocyclic ligands⁴ and Nelson et al. have reported on silver(I) and cadmium(II) complexes containing N_3P_2 pentadentate macrocyclic ligands.⁵ In the preparation of these metal complexes, the appropriate phosphine amine, 2,6-diacetylpyridine, and metal ion, in 1:1:1 ratios, were refluxed in alcoholic solutions for various lengths of times.

We now wish to report the first synthesis and characterization of the two new macrocyclic Schiff base diphosphine diamine complexes $[\text{Ni}(\text{Me}_2[14]\text{dienatoN}_2\text{P}_2)]\text{PF}_6$ (I) and $[\text{Ni}(\text{Me}_2[16]\text{dieneN}_2\text{P}_2)](\text{PF}_6)_2$ (II). In addition, we have completed the X-ray structural determination of $[\text{Ni}(\text{Me}_2[16]\text{dieneN}_2\text{P}_2)](\text{PF}_6)_2 \cdot 0.5\text{H}_2\text{O}$.⁶

Experimental Section

Reagents. Phenylphosphine was obtained from either Strem Chemical Co. or Pressure Chemical Co. and was used as received. The amine salts 2-chloroethylamine hydrochloride and 3-chloropropylamine hydrochloride were purchased from Aldrich Chemical Co. and used as received. All other organic starting materials, solvents, and metal salts were reagent grade commercial materials. The organic starting materials were distilled under nitrogen to ensure purity. The



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solvents were dried with either lithium aluminum hydride or sodium metal, distilled under nitrogen, and then degassed prior to use.

All reactions in the synthesis of the ligands and metal complexes were carried out under a nitrogen atmosphere with use of Schlenk type airless ware. Standard techniques were employed for the manipulation of air-sensitive compounds. All transfers were completed by using syringes that were flushed with nitrogen before use or by using stainless-steel transfer tubes, rubber septums, and a positive nitrogen pressure. Minute traces of water and oxygen were removed from commercially available prepurified nitrogen by passage of the gas through two 40 × 3 in. columns packed with Drierite and hot (180

Table I. NMR and Visible Spectral Data

compd in soln ^c	³¹ P { ¹ H} NMR ^a		¹ H NMR ^b		electronic spectra, cm ⁻¹ × 10 ³
	δ _P	δ _{Ph}	δ _{CH₂}	δ _{other}	
CH ₂ (CH ₂ P(Ph)(CH ₂) ₂ NH ₂) ₂	-28.8, -28.9	7.3	2.7 (m), 1.7 (m)	NH ₂ 1.7 (br)	
CH ₂ (CH ₂ P(Ph)(CH ₂) ₃ NH ₂) ₂	-25.8, -26.0	7.4	2.7 (m), 1.6 (m)	NH ₂ 1.6 (br)	
[Ni(Me ₂ [14]dienatoN ₂ P ₂)]PF ₆	52.8	7.4-8.0	1.3-3.4	γ-CH 5.3 (s) CH ₃ 2.2 (s)	23.3 (631), 29.9 (8229) (MeOH), 23.3, 29.4 (solid state)
[Ni(Me ₂ [16]dieneN ₂ P ₂)](PF ₆) ₂	-4.3	7.3-7.9 (m)	3.8-4.0 (m) 2.1-2.8 (m)	CH ₂ 4.7 (s) CH ₃ 2.5 (s)	26.3 (606) (acetone), 25.6 (solid state)

^a Phosphorus-31 chemical shifts are in ppm relative to 85% H₃PO₄ with negative values being upfield from the reference. ^b Proton chemical shifts are in ppm relative to internal Me₄Si. ^c The solvent was (CD₃)₂CO in all cases except for the ³¹P spectrum of 3,3,3-N₂P₂ (benzene) and the ¹H and ³¹P spectra of the 14-membered ring complex (CD₃NO₂).

°C) BASF active copper catalyst, respectively.

(A) **Synthesis of Phosphorus Compounds.** 1. **Ph(H)PCH₂CH₂NH₂ and Ph(H)PCH₂CH₂CH₂NH₂.** A solution containing 15.2 g (0.14 mol) of phenylphosphine dissolved in 30 mL of THF was added dropwise with stirring at 0 °C to 3.4 g (0.15 mol) of sodium metal in 30 mL of THF. During the addition, the solution turned orange, and H₂ gas evolved. After the addition was complete, the mixture was warmed to 25 °C and stirred for 6 h. Next ~0.14 mol of 2-chloroethylamine, dissolved in diethyl ether, was added dropwise at 0 °C until the orange solution turned colorless. The NaCl that precipitated during the reaction was removed by filtration, and the bidentate ligand ((2-aminoethyl)phenylphosphine) was recovered by vacuum distillation at 64 °C (0.10 torr). The yield based on phenylphosphine was 38%. The ligand was characterized by infrared and ¹H NMR spectra (see Table I). The same procedure was used to prepare (3-aminopropyl)phenylphosphine with 3-chloropropylamine. The ligand was vacuum-distilled (<1 torr) at 86 °C. The yield based on phenylphosphine was 55%. The ligand was characterized by infrared and ¹H NMR spectra.

The 2-chloroethylamine was prepared in situ by neutralizing 2-chloroethylamine hydrochloride in H₂O with NaOH at ~0 °C. The 2-chloroethylamine was then extracted with diethyl ether, and the solution was dried over 3-Å molecular sieves and subsequently purged with N₂ for 30 min before being used. The same procedure was used to isolate 3-chloropropylamine. Particularly, the free 2-chloroethylamine should be kept cool, used soon after isolation, and considered to be quite toxic.

2. **CH₂[CH₂P(Ph)CH₂CH₂NH₂]₂, 2,3,2-N₂P₂, and CH₂[CH₂P(Ph)CH₂CH₂CH₂NH₂]₂, 3,3,3-N₂P₂.** A solution containing 8.1 g (53 mmol) of (2-aminoethyl)phenylphosphine dissolved in 30 mL of THF was added dropwise with stirring at 0 °C to 1.3 g (56 mmol) of sodium metal in 30 mL of THF. After the addition was complete, the orange solution was warmed to 25 °C and stirred for 6 h. Next, 2.98 g (26 mmol) of 1,3-dichloropropane dissolved in 30 mL of THF was added dropwise with stirring at 0 °C until the orange solution was colorless. At that point the solution was warmed to 25 °C and stirred for 3 h. The THF was removed by distillation and replaced with diethyl ether, which precipitated the NaCl. The NaCl was removed by filtration, and the solvent was removed under vacuum to give a colorless oil (yield 66%). The resultant ligand was characterized by infrared and ¹H NMR spectra.

The 3,3,3-N₂P₂ ligand was prepared in 77% yield by the above procedure with (3-aminopropyl)phenylphosphine; it was characterized by infrared and ¹H NMR spectra.

(B) **Synthesis of Schiff Base Diphosphine Diamine Macrocyclic Complexes.** 1. **[Ni(Me₂[14]dienatoN₂P₂)]PF₆.** Acetylacetone (Hacac) (0.60 mL, 5.8 mmol) in 10 mL of MeOH was added dropwise with stirring at 20 °C to 1 g (2.9 mmol) of 2,3,2-N₂P₂ dissolved in 30 mL of methanol. The colorless solution was refluxed for 16 h, during which time it turned light yellow. Next, 0.71 g (2.9 mmol) of Ni(OAc)₂·4H₂O dissolved in 30 mL of MeOH was added dropwise with stirring at 20 °C, and the solution was refluxed for 16 h. A dark (almost opaque) red-brown solution resulted.

Approximately 90% of the methanol was then removed by distillation and replaced with 60 mL of deaerated H₂O that had been acidified to pH 4 with acetic acid. The Ni(II) complex was only slightly soluble in water; however, as the solution was refluxed, the compound gradually dissolved and the solution changed from a dark red-brown to a light orange color. The PF₆ salt was isolated after adding 0.97 g (58 mmol) of NaPF₆ dissolved in 50 mL of H₂O to the orange solution. The resulting orange powder was purified by

column chromatography with basic alumina as the support and 95% EtOH as the eluant. The complex [Ni(Me₂[14]dienatoN₂P₂)]PF₆ was isolated in 30% yield. Anal. Calcd for C₂₄H₃₁F₆N₂NiP₂: C, 47.00; H, 5.09; N, 4.56; P, 15.15; Ni, 9.57. Found: C, 47.21; H, 5.20; N, 4.70; P, 15.23; Ni, 9.77.

2. **[Ni(Me₂[16]dieneN₂P₂)](PF₆)₂.** This complex was prepared according to the above procedure by using 3,3,3-N₂P₂ as the tetradentate ligand. On cooling of the concentrated orange solution, the diene complex was isolated as yellow crystals at pH 4.0. Purification was accomplished by redissolving the crude product in the minimum amount of acetone and putting it on a silica gel column. The complex was eluted with nitromethane. Upon removal of the solvent, the complex was recrystallized from an acetone/H₂O mixture. The H₂O was adjusted to pH 4 with acetic acid, and long yellow crystals were isolated. Anal. Calcd for C₂₆H₃₆F₁₂N₂NiP₄: C, 39.67; H, 4.61; N, 3.56. Found: C, 40.24; H, 4.76; N, 3.73.

(C) **Physical Measurements.** Elemental analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach, West Germany, and Midwest Microlabs, Indianapolis, Ind. The samples were dried in vacuo at 100 °C for at least 5 h before analysis.

A Perkin-Elmer Model 457 infrared spectrophotometer was used to record the infrared spectra. Polystyrene was used as a standard to calibrate each Nujol mull spectrum.

Visible and ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer. Electronic absorption spectra of the complexes in solution were obtained in matched 5.0-, 1.0-, and 0.1-cm quartz cells, and the solid-state spectra were recorded by the diffuse transmittance technique.⁷

Conductivities were calculated from resistance measurements on ~10⁻³ M solutions with use of a Yellow Springs Instruments Model 31 conductivity bridge.

Magnetic susceptibilities of the complexes were measured with use of a Faraday apparatus. The susceptibilities of the ligands were calculated from Pascal's constants.⁸ Values reported are averages of measurements made at field strengths of 7 and 5 kG.

Proton magnetic resonance spectra were collected on a Varian A60A or an EM 360 spectrometer with Me₄Si as an internal standard. Fourier-mode, proton-noise-decoupled phosphorus-31 NMR spectra were collected at ~30 °C on a Bruker HX-90 spectrometer operating at 36.43 MHz. For the ³¹P spectra, 10-mm tubes with concentric 5-mm inserts (containing the deuterium lock and trimethyl phosphate as a secondary standard) were used; the chemical shifts are reported relative to 85% H₃PO₄ and are reproducible to ±0.05 ppm. Positive chemical shifts are downfield from 85% H₃PO₄.

(D) **Crystal Structure Determination of [Ni(Me₂[16]dieneN₂P₂)](PF₆)₂·0.5H₂O.** Collection and Reduction of Data. Straw yellow crystals of the complex were grown from an acetone/H₂O solution. We experienced considerable difficulties in obtaining suitable crystals; most crystals were very thin and not well developed. The data crystal used in this study had dimensions 0.08 × 0.26 × 1.6 mm; diffraction characteristics of this crystal are poor, the crystal has broad reflection profiles (0.25° half-height width for reflections with 2θ = 2θ), and the intensities of the reflections decrease rapidly with increasing angle θ. This may result from inhomogeneity in the water content in the volume of the crystal.

Precession photographs taken with Cu Kα radiation showed Laue symmetry 2/m, and systematic extinctions (*h*0*l* with *l* = odd and 0*kl*

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with $k = \text{odd}$) indicated space group $P2_1/c$. More exact unit cell dimensions were obtained from measurements on a computer-controlled Syntex PI diffractometer by use of Mo $K\alpha$ radiation and a least-squares refinement. Unit cell dimensions based on 12 reflections having $10.5^\circ < 2\theta < 21.1^\circ$ are as follows: $a = 14.049$ (12) Å, $b = 12.367$ (8) Å, $c = 20.129$ (9) Å, and $\beta = 105.11$ (5)° ($T = 20$ (1) °C). The observed density was 1.53 (1) g/cm³, which is in good agreement with the calculated density of 1.55 g/cm³ based on 4 chemical units per unit cell.⁹

Data collection for the crystal structure determination was carried out on a Picker FACS-I diffractometer with use of filtered Mo $K\alpha$ radiation and a θ - 2θ scan. The broad reflections necessitated large scan widths and relatively slow scanning speeds (scan width = $(1.4 + 0.7 \tan \theta)^\circ$, scanning speed = 1° min^{-1}). The scanning speed together with scan width permitted us to measure some 5000–6000 reflections in the time allotted to this experiment. Examination of a sample of reciprocal space for $37^\circ < 2\theta < 47^\circ$ indicated that of the 2500 reciprocal lattice points in this range only about 500 would generate reflections of significant intensity. Considering the requirements of least-squares refinements, we decided to measure each independent reflection twice (in two quadrants) in the range $0^\circ < 2\theta < 37^\circ$ rather than to measure reflections with only single coverage in the range $0^\circ < 2\theta < 47^\circ$. The data set obtained in this way contains 2600 independent reflections (compared with 3100 independent reflections if we had used the second alternative), but each independent reflection has σ lowered by the factor $2^{1/2}$.

The stability of the crystal under irradiation and the overall stability of intensity measurements was monitored by measuring 2 standard reflections for each 50 reflections of the data set. Automatic alignment checks and correction (if necessary) were performed after each 500 reflections. No radiation damage of the crystal was observed. Altogether 5542 reflections were measured; after they were corrected for absorption and averaged, the unique set contained 2626 reflections. From this number 2230 reflections had intensity larger than 1σ and they were used in the refinement.¹⁰

Solution and Refinement of the Structure. Intensities were converted to structure factors and put on an absolute scale by using standard computer programs.¹¹ Intensity statistics confirmed the space group $P2_1/c$. The coordinates of the nickel atoms were determined from a three-dimensional Patterson map. A series of successive electron density calculations disclosed the positions of the P atoms and finally of all atoms (except hydrogens) in the crystal structure. Atomic scattering factors for neutral Ni, P, F, N, and C used in this paper are those calculated by Cromer and Mann,¹² and atomic scattering factors of hydrogen are from Stewart, Davidson, and Simpson.¹³ Correction for the anomalous scattering of nickel was taken from ref 14.

The least-squares refinement on F was performed in several steps: (a) Mixed temperature factors (C and N atoms isotropic), H contributions neglected, gave $R = 0.108$. (b) Mixed temperature factors (C and N atoms isotropic), H contributions included (but not refined, $C-H = 1.08$ Å), gave $R = 0.097$ and $R_w = 0.102$. (c) Anisotropic temperature factors for all atoms except H, H contributions included (but not refined), gave $R = 0.078$. (d) A peak observed on a difference map after step c was concluded was interpreted as a water molecule, and its oxygen atom was included in the refinement. The population parameter of H₂O was found to be 0.45; $R = 0.076$ and $R_w = 0.082$.

In all these steps weights of the type $1/\sigma^2$ gave more inferior

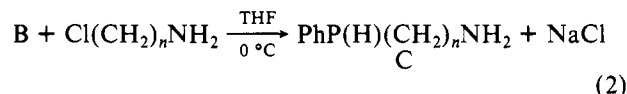
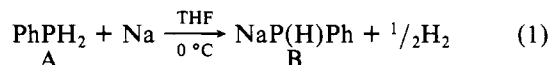
uniformity of $\langle w(\Delta F)^2 \rangle$ than weights given by $w = (F_o/40)^2$ if $F_o < 40$ and $w = (40/F_o)^2$ otherwise; all results quoted here are based on this weighting scheme (compare with that of Cruickshank¹⁵). Hamilton's test of statistical significance¹⁶ was applied on our model b and on our model d. Despite the fact that the last model has only 5.4 reflections per least-squares parameter, it is significant on a confidence level of better than 0.005.

The final R factor 0.076 may seem to be higher than expected for a well-refined structure, but close examination of other papers on complexes containing BF_4^- or PF_6^- ions indicate that a high R factor is common: for example, in ref 17, with two PF_6^- ions per complex unit, $R = 0.095$; in ref 18, with two BF_4^- ions per complex unit, $R = 0.073$; in ref 19, with one BF_4^- ion per complex unit $R = 0.078$, etc. This is probably related to either partial rotational disorder of BF_4^- and PF_6^- groups or to their large amplitudes of oscillations, which are indicated by unusually large temperature coefficients of F atoms as shown in our work and in the three quoted papers. In each case, the conventional structure factor, where temperature motion is represented in harmonic approximation, does not adequately express the scattering by these atoms.

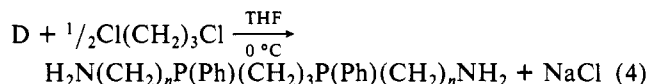
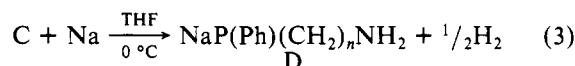
Table II contains positional and thermal parameters based on step d of our least-squares refinement. Bond lengths and angles within the cationic macrocycle are given in Tables III and IV; equations of least-squares planes are in Table V, and the dihedral angles are in Table VI.

Results and Discussion

Synthesis and Physical Properties. Synthesis of $[\text{Ni}(\text{Me}_2[14]\text{dienatoN}_2\text{P}_2)]\text{PF}_6$ and $[\text{Ni}(\text{Me}_2[16]\text{dieneN}_2\text{P}_2)](\text{PF}_6)_2$ first required preparation of the linear tetradentate diphosphine diamine ligands, trimethylenebis[(2-aminoethyl)phenylphosphine] (2,3,2- N_2P_2) and trimethylenebis[(3-aminopropyl)phenylphosphine] (3,3,3- N_2P_2) as described by Isslieb.²⁰ The reaction sequence is given in eq 1–4. The procedures used



where $n = 2, 3$

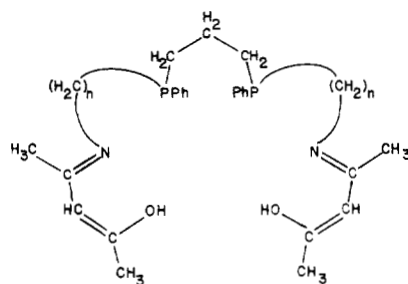


were similar to those of Isslieb except that THF was chosen as the solvent instead of liquid NH_3 .

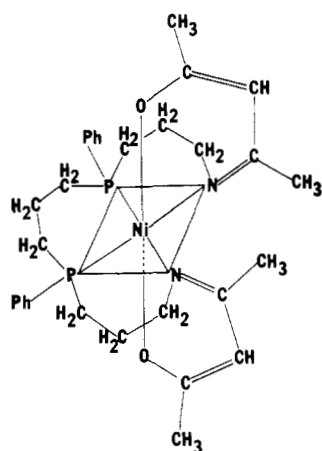
Attempted syntheses of the macrocyclic complexes by the in situ reaction of the diphosphine diamine tetradentate ligand, Hacac, and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in aqueous solution, analogous to the method we developed earlier for tetraaza systems,²¹ proved unsuccessful. Therefore, we used an alternate method, which required synthesis of the linear, sexidentate Schiff base ligands bis(acetylacetonate) trimethylenebis[(2-aminoethyl)phenylphosphine] (III, $n = 2$) and bis(acetylacetonate) trimethylenebis[(3-aminopropyl)phenylphosphine] (III, $n = 3$) by condensation of 2 equiv of Hacac with 1 equiv of the ap-

- (9) It is interesting to consider how the unit cell "constants" are affected by a change of water content in the unit cell. With a space requirement of $24 \text{ Å}^3/\text{H}_2\text{O}$ molecule and with a unit cell volume of 3408 Å^3 , changes in the water content by 0.1 molecule/complex unit causes isotropic changes of unit cell edge by 0.012 Å (the average content in our crystal is 0.45 molecule/chemical unit from the least-squares refinement).
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III



IV

appropriate diphosphine diamine in methanol. Formation of the sexidentate Schiff base ligand at this stage was confirmed by a ^1H NMR spectrum, which gave the following peaks: 7.6–7.3 (5), m, Ph; 4.9 (1), s, $=\text{CH}$; 3.5–3.0 (2), m, CH_2 adjacent to $\text{C}=\text{N}$; 2.1–1.6 (13), m, remaining CH_2 and CH_3 protons. The two macrocyclic complexes were isolated from aqueous solution as orange and yellow PF_6^- derivatives. The successful syntheses presumably involve acid-catalyzed intramolecular rearrangement of a six-coordinate Schiff base $\text{Ni}(\text{II})$ complex. One form is shown in structure IV. This species was never isolated, but other work in our laboratory has resulted in the isolation of $\text{Co}(\text{III})$ complexes of this type.²² Rearrangement would require the elimination of 1 equiv of Hacac as the ring is closed. We have suggested that a similar mechanism is operative in the synthesis of tetraaza macrocycles; however, in these cases, the sexidentate precursors were always isolated before further reaction.²³

Purification was handled differently for each complex. The complex containing the 14-membered dienato ring was purified with use of a basic alumina column with 95% EtOH as the eluant. The complex was soluble in acetone, methanol, and ethanol. Attempts to obtain single crystals suitable for X-ray analysis have failed. Purification of the complex with the 16-membered ring was accomplished with use of a silica gel column with CH_3NO_2 as the eluant, followed by recrystallization from an acetone/ H_2O mixture. The solution was adjusted to pH 4 with HOAc. Purification attempts using acidic, neutral, or basic alumina resulted in decomposition of the diene complex.

Although the general method of synthesis was the same for both the 14- and the 16-membered ring macrocyclic complexes and each was isolated at pH ~ 4 , it is interesting to note that the 14-membered ring complex was isolated in the dienato form, I, while the 16-membered ring is in the diene form, II. Attempts to convert the 14-membered ring to its diene analogue by careful adjustment of the pH resulted in decompo-

sition of the product. Conversion of the 16-membered ring diene complex to the dienato form was not attempted.

Characterization. The two new macrocyclic complexes were characterized by elemental analyses, conductivity and magnetic susceptibility measurements, and visible, infrared, and NMR spectra. In addition, a single-crystal structure determination of $[\text{Ni}(\text{Me}_2[16]\text{dieneN}_2\text{P}_2)](\text{PF}_6)_2 \cdot 0.5\text{H}_2\text{O}$ has been completed.

The infrared spectra indicate that macrocyclic ring formation has occurred in both complexes since bands attributable to NH_2 and $>\text{C}=\text{O}$ stretching vibrations are absent while bands assignable to $\text{C}=\text{N}$ (diene) or $\text{C}=\text{N}$ and $\text{C}=\text{C}$ (dienato) stretching vibrations at 1670 and 1540 cm^{-1} , respectively, are present. Bands due to the PF_6^- are not split and occur as two strong, sharp absorptions at ~ 840 and 565 cm^{-1} . These data suggest that the PF_6^- anions are not coordinated.

Results of conductivity measurements in acetone and methanol indicate that the diene ($\Lambda_M = 212 \text{ mhos cm}^2/\text{mol}$) and dienato ($\Lambda_M = 92 \text{ mhos cm}^2/\text{mol}$) complexes are 2:1 and 1:1 electrolytes, respectively.²⁴ Both complexes are low spin, with μ_{eff} equal to 0.90 (diene) and 0.39 μ_B (dienato). These data, along with the electronic spectra (vide infra), indicate that both complexes are planar and four-coordinate.

Visible spectra of the macrocyclic complexes obtained in both solution and the solid state (diffuse transmittance) were very similar, indicating no change in the inner coordination sphere. The single band for each complex at 23.3×10^3 (dienato) or $26.3 \times 10^3 \text{ cm}^{-1}$ (diene) is consistent with results published by Sacconi for square-planar $\text{Ni}(\text{II})$ complexes where the N_2P_2 tetradentate ligand was *N,N*-bis(2-(diphenylphosphino)ethyl)-*N,N*-dimethylethylenediamine (PNPN).²⁵

Two diastereoisomers, the meso and the *dl* pair, are possible for each of the N_2P_2 tetradentate ligands arising from the presence of the two equivalent but asymmetric phosphorus atoms. The presence of two singlets (Table I) in the $^{31}\text{P}\{^1\text{H}\}$ spectrum of each ligand is consistent with this assignment. King et al. have reported a similar occurrence of two isomers of the linear tetrakis(tertiary phosphine) $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2$. These isomers have widely differing solubilities and melting points,²⁶ which allowed their separation. No attempt has been made to separate the N_2P_2 mixture discussed herein; however, the two macrocyclic complexes give single phosphorus peaks at 52.8 and -4.3 ppm for the 14- and 16-membered ring complexes, which suggests that only one isomer of each exists in solution. X-ray analysis of the 16-membered ring complex showed that this is the meso isomer.

It is interesting to note that chemical shifts observed for the phosphorus peaks in the two macrocycles are either upfield (-4.3 ppm) or downfield (52.8 ppm) from H_3PO_4 , depending on the chelate ring size. It has been generally observed that when P is part of a five-membered chelate ring, the phosphorus resonance is shifted downfield relative to the resonance position for a comparable P group in a six-membered chelate ring. Slack et al. have observed such effects for 5- and 6-membered rings in $\text{Pt}(\text{II})$ complexes using 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp).²⁷ The chemical shifts reported for those phosphorus resonances were 41.1 (PtCl_2dppe) and -5.6 ppm (PtCl_2dppp).

The physical data indicate that the coordination geometry of both the 14- and 16-membered ring macrocyclic complexes is planar. X-ray analysis of $[\text{Ni}(\text{Me}_2[16]\text{dieneN}_2\text{P}_2)]-$

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations^a

atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ni	0.1813 (1)	0.3083 (1)	0.45836 (7)	0.0462 (9)	0.0440 (9)	0.0360 (9)	0.0055 (8)	0.0061 (7)	0.0008 (8)
P1	0.2923 (2)	0.2472 (3)	0.5474 (2)	0.056 (2)	0.070 (2)	0.040 (2)	0.018 (2)	0.001 (2)	0.002 (2)
P2	0.1243 (2)	0.1451 (2)	0.4311 (2)	0.064 (2)	0.038 (2)	0.043 (2)	0.009 (2)	0.018 (2)	0.002 (2)
P3	0.3752 (3)	0.6514 (4)	0.2294 (2)	0.083 (3)	0.108 (4)	0.077 (3)	-0.004 (3)	0.033 (3)	-0.025 (3)
P4	0.0089 (3)	0.7021 (3)	0.4030 (2)	0.077 (3)	0.063 (3)	0.070 (3)	0.004 (2)	0.024 (3)	-0.015 (2)
F1	0.4242 (8)	0.5833 (11)	0.2944 (6)	0.141 (9)	0.225 (12)	0.138 (9)	0.022 (9)	0.003 (7)	0.062 (10)
F2	0.4175 (11)	0.5838 (12)	0.1813 (8)	0.261 (16)	0.193 (13)	0.243 (15)	-0.000 (12)	0.152 (14)	-0.051 (12)
F3	0.3236 (11)	0.7156 (13)	0.1665 (7)	0.240 (14)	0.246 (17)	0.163 (12)	0.050 (12)	0.046 (11)	0.109 (12)
F4	0.3155 (13)	0.7049 (11)	0.2715 (7)	0.353 (20)	0.197 (14)	0.171 (11)	0.128 (14)	0.139 (13)	0.001 (10)
F5	0.4594 (12)	0.7246 (15)	0.2424 (8)	0.252 (16)	0.344 (22)	0.232 (15)	-0.241 (17)	-0.036 (14)	0.012 (15)
F6	0.2903 (10)	0.5647 (12)	0.2147 (6)	0.203 (12)	0.252 (15)	0.156 (10)	-0.122 (12)	0.076 (9)	-0.037 (10)
F7	0.0939 (8)	0.7511 (10)	0.4606 (5)	0.137 (8)	0.193 (10)	0.110 (8)	-0.027 (8)	0.020 (7)	-0.024 (7)
F8	0.0767 (7)	0.7058 (9)	0.3528 (5)	0.137 (7)	0.190 (10)	0.144 (8)	-0.010 (7)	0.102 (7)	-0.048 (8)
F9	-0.0614 (6)	0.7020 (7)	0.4532 (4)	0.134 (7)	0.098 (16)	0.119 (7)	0.017 (5)	0.087 (6)	0.003 (5)
F10	-0.0706 (8)	0.6546 (14)	0.3484 (6)	0.135 (9)	0.379 (22)	0.124 (9)	-0.070 (11)	0.034 (8)	-0.100 (11)
F11	-0.0206 (8)	0.8223 (9)	0.3839 (6)	0.171 (9)	0.124 (9)	0.198 (11)	0.054 (7)	0.113 (9)	0.077 (8)
F12	0.0455 (8)	0.5892 (8)	0.4273 (7)	0.175 (10)	0.074 (7)	0.276 (14)	0.052 (7)	0.095 (10)	0.037 (8)
Ow ^b	0.6074 (20)	0.8444 (21)	0.2167 (15)	0.168 (27)	0.154 (26)	0.187 (29)	-0.071 (29)	0.111 (22)	-0.048 (20)
N1	0.2336 (7)	0.4518 (7)	0.4754 (4)	0.075 (7)	0.051 (7)	0.045 (6)	-0.001 (5)	0.007 (5)	-0.016 (5)
N2	0.0924 (6)	0.3652 (6)	0.3768 (4)	0.045 (5)	0.040 (6)	0.052 (6)	0.007 (5)	0.009 (5)	-0.001 (5)
C1	0.2492 (14)	0.5037 (16)	0.5431 (10)	0.059 (14)	0.063 (15)	0.060 (14)	0.001 (11)	-0.006 (12)	-0.017 (12)
C2	0.3389 (17)	0.4615 (19)	0.5951 (11)	0.096 (18)	0.088 (18)	0.060 (15)	-0.006 (14)	0.001 (14)	-0.029 (13)
C3	0.3254 (8)	0.3463 (11)	0.6169 (6)	0.058 (8)	0.089 (11)	0.055 (8)	0.014 (7)	-0.005 (7)	-0.020 (7)
C4	0.2645 (9)	0.1281 (11)	0.5930 (6)	0.091 (10)	0.084 (11)	0.031 (7)	0.030 (8)	0.005 (7)	0.002 (8)
C5	0.2299 (10)	0.0344 (10)	0.5476 (6)	0.104 (11)	0.062 (10)	0.043 (8)	0.038 (8)	0.025 (8)	0.025 (8)
C6	0.1284 (10)	0.0469 (9)	0.4989 (6)	0.088 (10)	0.043 (8)	0.051 (8)	0.006 (7)	0.011 (8)	0.014 (6)
C7	-0.0079 (8)	0.1449 (10)	0.3901 (6)	0.037 (7)	0.079 (9)	0.060 (8)	-0.018 (6)	-0.019 (6)	0.010 (7)
C8	-0.0414 (14)	0.2297 (16)	0.3352 (10)	0.069 (14)	0.066 (17)	0.060 (14)	-0.003 (12)	-0.004 (12)	-0.014 (12)
C9	-0.0137 (13)	0.3444 (15)	0.3626 (10)	0.047 (12)	0.061 (15)	0.068 (14)	0.020 (11)	0.008 (11)	0.000 (12)
C10	0.1261 (14)	0.4201 (14)	0.3346 (9)	0.068 (15)	0.041 (12)	0.046 (13)	-0.000 (11)	0.011 (11)	-0.005 (10)
C11	0.2325 (15)	0.4534 (15)	0.3572 (10)	0.081 (17)	0.052 (14)	0.054 (14)	-0.005 (12)	0.028 (12)	0.016 (11)
C12	0.2599 (14)	0.5034 (17)	0.4277 (10)	0.053 (13)	0.078 (17)	0.055 (14)	-0.004 (12)	0.007 (11)	-0.007 (13)
C13	0.4053 (8)	0.2137 (10)	0.5255 (5)	0.043 (7)	0.092 (11)	0.041 (7)	0.011 (7)	-0.001 (6)	0.005 (7)
C14	0.4220 (19)	0.2522 (26)	0.4671 (12)	0.096 (18)	0.206 (31)	0.074 (17)	0.092 (21)	0.039 (16)	0.012 (18)
C15	0.5034 (26)	0.2285 (35)	0.4423 (15)	0.118 (25)	0.269 (44)	0.071 (20)	0.079 (30)	0.031 (19)	0.015 (24)
C16	0.5704 (21)	0.1641 (25)	0.4806 (20)	0.085 (22)	0.091 (23)	0.125 (26)	0.007 (17)	0.025 (22)	-0.028 (20)
C17	0.5622 (18)	0.1271 (25)	0.5412 (22)	0.045 (18)	0.128 (27)	0.183 (35)	0.037 (16)	0.013 (21)	0.030 (25)
C18	0.4782 (19)	0.1537 (21)	0.5632 (14)	0.073 (18)	0.118 (23)	0.121 (22)	0.012 (17)	0.005 (17)	0.049 (18)
C19	0.1811 (8)	0.0782 (11)	0.3720 (6)	0.062 (8)	0.058 (11)	0.035 (7)	0.021 (7)	0.018 (7)	0.006 (8)
C20	0.2371 (16)	0.1349 (11)	0.3386 (8)	0.264 (22)	0.045 (10)	0.108 (13)	0.013 (12)	0.143 (16)	-0.011 (9)
C21	0.2835 (17)	0.0902 (17)	0.2945 (10)	0.277 (26)	0.065 (13)	0.165 (19)	-0.009 (14)	0.172 (19)	-0.015 (13)
C22	0.2738 (14)	-0.0185 (18)	0.2816 (8)	0.152 (15)	0.116 (18)	0.067 (10)	0.019 (13)	0.071 (11)	0.003 (11)
C23	0.2205 (12)	-0.0787 (12)	0.3142 (9)	0.111 (12)	0.070 (11)	0.082 (11)	0.031 (10)	0.020 (10)	-0.032 (10)
C24	0.1727 (9)	-0.0306 (12)	0.3597 (7)	0.075 (9)	0.039 (10)	0.097 (11)	0.011 (8)	0.022 (9)	-0.019 (9)
C25	0.0682 (16)	0.4607 (18)	0.2654 (9)	0.103 (17)	0.089 (17)	0.032 (13)	0.024 (14)	-0.004 (13)	0.026 (12)
C26	0.3123 (17)	0.6114 (17)	0.4340 (13)	0.085 (16)	0.053 (16)	0.139 (21)	-0.054 (14)	0.031 (16)	-0.011 (15)

^a The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. ^b The populational parameter of the disordered water molecule is 0.47 (3).

Table III. Bond Lengths within the Cationic Macrocyclic^a

Ni-N1	1.916 (9)	Ni-N2	1.918 (8)
Ni-P1	2.182 (3)	Ni-P2	2.188 (4)
N1-C1	1.47 (2)	N2-C9	1.46 (2)
C1-C2	1.51 (3)	C9-C8	1.53 (3)
C2-C3	1.52 (3)	C8-C7	1.51 (2)
C3-P1	1.83 (1)	C7-P2	1.83 (1)
P1-C4	1.83 (1)	P2-C6	1.82 (1)
C4-C5	1.48 (2)	C6-C5	1.51 (2)
N1-C12	1.29 (2)	N2-C10	1.27 (2)
C12-C11	1.50 (3)	C10-C11	1.50 (3)
C12-C26	1.51 (3)	C10-C25	1.50 (2)
P1-C13	1.81 (1)	P2-C19	1.80 (1)
C13-C14	1.34 (3)	C19-C20	1.36 (2)
C14-C15	1.39 (5)	C20-C21	1.35 (3)
C15-C16	1.32 (5)	C21-C22	1.37 (3)
C16-C17	1.34 (6)	C22-C23	1.34 (3)
C17-C18	1.40 (5)	C23-C24	1.40 (2)
C18-C13	1.33 (3)	C24-C19	1.37 (2)

^a The number in parentheses following each datum is the estimated standard deviation in the last significant figure.

(PF₆)₂·0.5H₂O confirms this geometry for the 16-membered species. The positional and thermal parameters for all atoms are given in Tables II and III. A table of observed and cal-

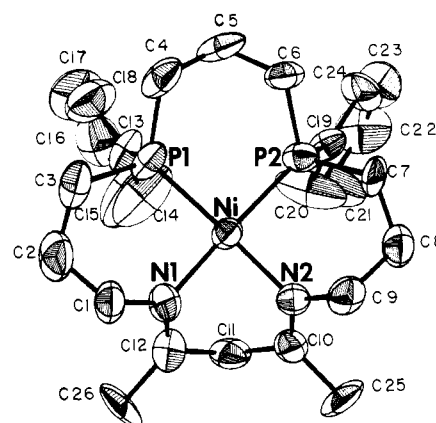


Figure 1. Above-the-plane view of the macrocyclic [Ni(Me₂[16]-dieneN₂P₂)]²⁺ cation.

culated structure factor amplitudes is available as supplementary material. Figure 1 is an ORTEP drawing that shows the above-the-plane view of the cation and the atomic numbering scheme used. From this view, the approximate C_s symmetry exhibited by the cation and the pseudo mirror plane containing

Table IV. Bond Angles within the Cationic Macrocycle^a

P1NiP2	91.3 (1)	N1NiN2	87.0 (3)
P1NiN1	90.9 (3)	P2NiN2	90.6 (3)
NiN1C1	121.9 (10)	NiN2C9	120.4 (9)
NiN1C12	119.9 (10)	NiN2C10	119.6 (9)
NiP1C3	112.4 (4)	NiP2C7	112.2 (4)
NiP1C4	119.3 (4)	NiP2C6	119.4 (4)
N1C1C2	112.9 (16)	N2C9C8	112.4 (15)
C1C2C3	112.4 (16)	C9C8C7	112.3 (14)
C2C3P1	115.8 (11)	C8C7P2	114.6 (10)
C3P1C4	101.6 (6)	C7P2C6	99.7 (6)
P1C4C5	113.7 (9)	P2C6C5	113.3 (9)
C4C5C6	115.0 (11)	C10C11C12	112.9 (18)
C1N1C12	118.2 (13)	C9N2C10	120.0 (12)
N1C12C11	116.5 (17)	N2C10C11	117.3 (14)
N1C12C26	127.2 (18)	N2C10C25	126.3 (17)
C26C12C11	116.2 (19)	C25C10C11	116.3 (17)
NiP1C13	111.2 (4)	NiP2C19	113.2 (5)
C3P1C13	106.1 (5)	C7P2C19	105.9 (5)
C4P1C13	104.9 (6)	C6P2C19	104.8 (6)
C13C14C15	125.9 (24)	C19C20C21	123.8 (15)
C14C15C16	116.5 (32)	C20C21C22	119.1 (21)
C15C16C17	121.5 (33)	C21C22C23	119.5 (19)
C16C17C18	119.2 (26)	C22C23C24	120.5 (16)
C17C18C13	122.2 (27)	C23C24C19	120.2 (14)
C18C13C14	114.5 (19)	C24C19C20	116.9 (13)

^a The number in parentheses following each datum is the estimated standard deviation in the last significant figure.

the Ni(II) ion and carbon atoms C5 and C11 are clearly visible. Comparison of the matched pairs of bond lengths and angles presented in Tables III and IV also reflects the near C_s symmetry for the cation. The Ni–P [2.182 (3), 2.188 (4) Å] and Ni–N [1.916 (9), 1.918 (8) Å] bond distances of the macrocyclic complex agree with other reported values for Ni(II) bonded to sp^3 P and sp^2 N atoms in a square-planar environment.^{25,28} The Ni(II) ion is displaced 0.07 Å out of the plane defined by the four donor atoms (plane 1) toward the side opposite the phenyl rings. Table V defines four least-squares planes and the deviation of the atoms from these planes.

Figure 2 shows a side view of the cation illustrating the cavity created by the phenyl rings and tilted diimine ring. The tilt of the diimine ring (plane 4) is 45.6° with respect to plane 1. C11 in the diimine ring is 0.56 Å above plane 4. Nelson has reported a similar folding ($41.8, 48.9^\circ$) for pentaaza macrocyclic 17-membered ring complexes that result from the condensation of the linear tetraamine (3,2,3- N_4) and 2,6-diacetylpyridine.²⁹ The acute angles reported by Nelson were measured from the intersection of the planes defined by the MN_4 unit and the pyridine ring.

The diimine ring exists in the boat conformation with two C=N bond distances of 1.27 (2) and 1.29 (2) Å. This com-

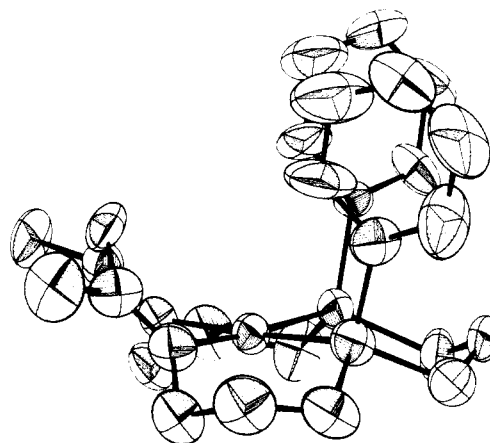


Figure 2. Side view of the macrocyclic cation.

pares to C=N bond distances of 1.285 (9) and 1.265 (9) Å found in the tetraaza macrocyclic complex $[Co(Me_2[14]dieneN_4) \cdot H_2O](PF_6)_2$. The difference in ring strain in the 16-membered ring macrocyclic complex compared to that in the 14-membered one is illustrated by distortion of the bond angle at the methylene carbon in the diimine ring. Puckering of this ring in the $[Ni(Me_2[16]dieneN_2P_2)]^{2+}$ system results in a bond angle of $113 (2)^\circ$, which is much closer to the expected sp^3 angle of 109.5° than the angle of $121.9 (7)^\circ$ that occurs in the more highly strained $[Co(Me_2[14]dieneN_4) \cdot H_2O]^{2+}$ system.¹⁷

Dihedral angles for the 16-membered ring Ni(II) complex are reported in Table VI. Deviations from the expected 60° angle for four atoms with T_d geometry suggest that the greatest ring strain occurs in the six-membered ring that contains the two phosphorus donor atoms.

Figure 3 provides a stereoscopic view of the molecular packing. The arrangement consists of the macrocyclic cation, with the PF_6^- anions all occupying general positions. The H_2O molecule is disordered with a population parameter of 0.47 (3). The positions of the two anions and H_2O molecule are outside the coordination sphere of the metal. There may be some hydrogen bonding between the H_2O molecule and F5, as the distance between the O atom and F5 is 2.72 (3) Å. F9 of one PF_6^- anion is positioned directly below the Ni(II) ion opposite the phenyl rings. F9 is 2.76 (1) Å from the Ni(II) ion, and the angle P4–F9–Ni is $177.3 (7)^\circ$. The two F9–Ni–P angles average $82.9 (4)^\circ$, and the two F9–Ni–N angles average 101.4° . The fluorine atom resides in a position consistent with a distorted square-pyramidal geometry. The Ni–F9 bond distance is longer than the Ni–Cl bond distance of 2.699 (7) Å observed for a 5-coordinate low-spin, square-pyramidal

Table V. Least-Squares Planes and Deviations Therefrom for $[Ni(Me_2[16]dieneN_2P_2)](PF_6)_2 \cdot 0.5H_2O$

Equations of the Planes ^a							
plane	<i>P</i>	<i>Q</i>	<i>R</i>	<i>S</i>	atoms defining plane		
I	−11.5969	1.9753	14.9602	5.2916	N1, N2, P1, P2		
II	5.0254	10.0048	7.2894	8.0323	C13, C14, C15, C16, C17, C18		
III	8.9578	−2.0211	11.4118	5.7133	C19, C20, C21, C22, C23, C24		
IV	−9.2005	9.3318	4.9299	4.4131	N1, N2, C10, C12		
Deviations from the Planes							
atom	dev, Å	atom	dev, Å	atom	dev, Å	atom	dev, Å
P1	−0.0033	N1	−0.0029	C13	−0.0263	C19	−0.0045
P2	0.0033	N2	0.0029	C14	0.0165	C20	0.0017
N1	0.0039	C10	−0.0030	C15	0.0075	C21	0.0055
N2	−0.0039	C12	0.0030	C16	−0.0209	C22	−0.0098
				C17	0.0094	C23	0.0071
				C18	0.0138	C24	0.0001

^a Equations are in the form $PX + QY + RZ = S$ with fractional coordinates X , Y , and Z lying along the a , b , and c axes, respectively.

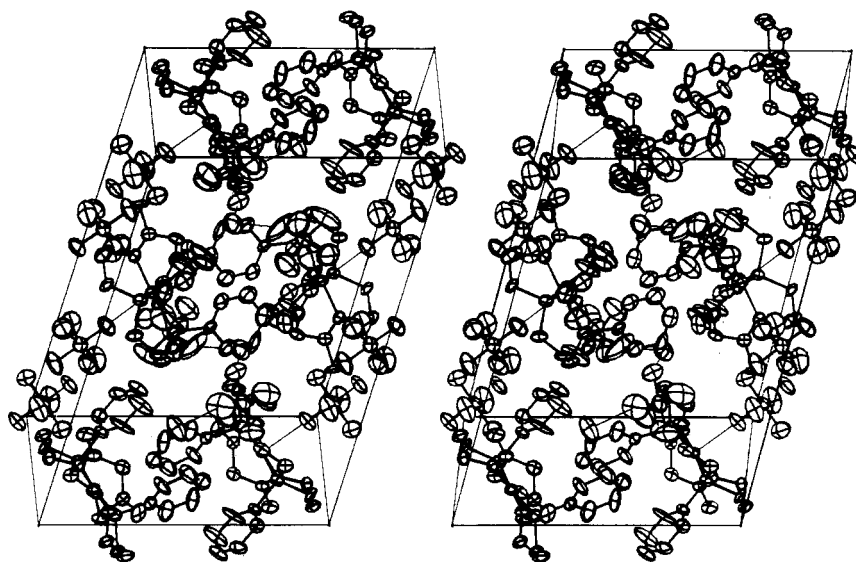


Figure 3. Stereoscopic view of the molecular packing for $[\text{Ni}(\text{Me}_2[16]\text{dieneN}_2\text{P}_2)](\text{PF}_6)_2 \cdot 0.5\text{H}_2\text{O}$. The a axis is horizontal to the right, the b axis is pointing toward the top of the page, and the c axis is the longest axis.

Table VI. Dihedral Angles for the 16-Membered Ring Complex^a

atoms defining angle				dihedral angle, deg
C3	C2	C1	N1	-70 (2)
C7	C8	C9	N2	71 (2)
P1	C3	C2	C1	56 (2)
P2	C7	C8	C9	-57 (2)
C6	C5	C4	P1	-70 (1)
C4	C5	C6	P2	70 (1)
C7	P2	C6	C5	-175 (1)
C3	P1	C4	C5	177 (1)
C4	P1	C3	C2	-171 (1)
C6	P2	C7	C8	173 (1)
C8	C9	N2	C10	102 (2)
C2	C1	N1	C12	-101 (2)
C9	N2	C10	C25	-6 (3)
C9	N2	C10	C11	171 (2)
C1	N1	C12	C26	4 (3)
C1	N1	C12	C11	-173 (1)
C26	C12	C11	C10	-129 (2)
C25	C10	C11	C12	128 (2)

^a The number in parentheses is the estimated standard deviation in the last significant figure.

Ni(II) complex with N_2P_2 donor atoms, which has also been synthesized in our laboratory.³⁰ Since the difference of the van der Waals radii between Cl and F is 0.45 Å, the Ni-F9 bond length is ~ 0.5 Å longer than what would be expected if there were any bonding interaction. The lack of any observed splitting of the bands assigned to absorptions of the PF_6^-

ions in the infrared spectrum, the conductivity data, and the visible spectrum also suggest no interaction between the Ni(II) ion and F9. Cunningham and Cummings obtained a similar result for $[\text{Co}(\text{Me}_2[14]\text{dieneN}_4) \cdot \text{H}_2\text{O}](\text{PF}_6)_2$.¹⁷ In the latter case, a fluorine atom of one PF_6^- ion was situated in an axial position 2.559 (10) Å below the Co(II) ion. Even though the F atom was aligned in the right position for bonding, the Co-F distance, which is ~ 0.5 Å longer than that reported for CoF_2 (2.10 Å), indicated minimal interaction.

Conclusion. A synthetic method has been developed for preparing transition-metal macrocyclic compounds with uninegative and neutral N_2P_2 Schiff base ligands. The scope of these reactions is currently under study in our laboratories. It is anticipated that some of the coordinated metal ions will cause the activation of selected small covalent molecules and thus will be useful in catalytic processes or as biochemical models.

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Supplementary Material Available: A listing of structure factor amplitudes ($\times 10$) (19 pages). Ordering information is given on any current masthead page.

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