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Synthesis and Characterization of Low-Spin Cobalt(II) Complexes with Macrocyclic Tetraaza Ligands. The Crystal Structure of $[Co([14]dieneN_4)\cdot H_2O](PF_6)_2$

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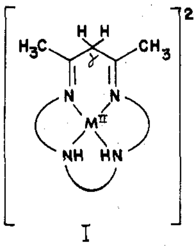
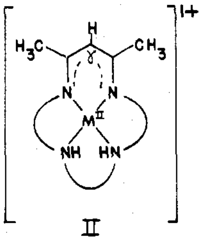
N,N'-Bis(2-aminoethyl)-1,3-propanediamine (2.3.2) condenses with 2,4-pentanedione (acac) in the presence of cobalt(II) ions to produce macrocyclic tetraaza ligands containing 14 ring members. Coordinated diene, I, and dieno, II, forms of the ligand have been isolated as Co(II) complexes with the following formulations: $[Co([14]dieneN_4)]X_2$ and $[Co([14]dienoN_4)]X$, where $X^- = PF_6^-$ and I^-, and $[Co([14]dieneN_4)][Co(NCS)_4]$. Magnetic and spectral data suggest that the anhydrous complexes in the solid state contain a square-planar Co(II) macrocyclic cation. In aqueous and methanol solutions, solvation of the cation occurs to produce octahedral coordination. The crystal and molecular structure of the monoaquo complex, $[Co([14]dieneN_4)\cdot H_2O](PF_6)_2$, was determined by single crystal x-ray diffraction techniques. The crystals form in the monoclinic space group $C2/c$ with $a = 22.482$ (3), $b = 16.741$ (2), $c = 15.572$ (2) Å, and $\beta = 131.59$ (2)° (λ 0.71069 Å). A total of 5023 independent reflections were measured on a Picker diffractometer using the θ–2θ scan technique with Zr-filtered Mo $K\alpha$ radiation. Refinement using 3064 reflections yielded a conventional R factor of 0.0953. The macrocyclic cation exhibits cis-meso symmetry and is essentially square pyramidal with the fifth coordination site occupied by the H_2O molecule ($Co–N_i = 1.915$; $Co–N_a = 1.988$; $Co–O = 2.283$ (9) Å). The presence of a weak $Co–PF_6$ interaction ($Co–F = 2.559$ (10) Å) in the sixth position is also indicated.

Introduction

Studies in our laboratories[1–4] over the past 5 years have shown that metal complexes containing 13-, 14- and 15-membered macrocyclic tetraaza ligands can be prepared via condensation of various linear polyamines with acetylacetone (or trifluoroacetylacetone) in the presence of Ni(II) and Cu(II) ions. Both isolation of the initial complexes and their interconversion between diene, I, and dieno, II, forms require careful adjustment of the solution pH, since the relative acidity of the γ bridge proton depends markedly on the nature of the metal ion and to a lesser extent on the size of the macrocyclic ring. For example, the pK_a of $Ni([14]dieneN_4)(PF_6)_2$ is 6.5 while that of $Cu([14]dieneN_4)(PF_6)_2$ is 9.3.



I



II

In order to gain a better understanding of the metal ion effects, we considered it desirable to try to synthesize the corresponding cobalt(II) complexes. Since all of the previously characterized Ni(II) and Cu(II) complexes were square planar, with the exception of a novel ligand coupled dimer which contains five-coordinate Ni(II),[5] the chances of isolating square-planar cobalt(II) complexes seemed good. Such complexes are of interest not only from the standpoint of their relative rarity but also because the coordinately unsaturated cobalt(II) ion in this macrocyclic environment may exhibit reactivity toward methylation or oxygenation as is characteristic of biologically active systems.[6–10]

Most cobalt(II) complexes which contain tetradentate ligands with nitrogen and/or oxygen donors are high-spin ($\mu_{eff} \simeq 4.9$–$5.2\ \mu_B$), five- or six-coordinate species. The extraplanar coordination sites are generally occupied by anionic ligands which are necessarily present to satisfy charge requirements or by solvent molecules. In order to stabilize four-coordinate, square-planar cobalt(II), various workers have found it necessary to react cobalt(II) ions with more rigid, macrocyclic, unsaturated ligands which have large ligand field strengths. Thus, Warner and Busch[11,12] and Endicott and co-workers[13,14] isolated the first examples of square-planar, low-spin cobalt(II) complexes via extension of the Curtis macrocyclization reactions. Busch and Long[15] also prepared a series of low-spin cobalt(II) complexes with a macrocyclic Schiff base ligand derived from 2,6-diacetylpyridine and 3,3'-diaminodipropylamine; however, these complexes proved to be trigonal bipyramidal due to coordination of one of the counterions. Other four- and five-coordinate cobalt(II) complexes have been synthesized by Musker and Steffen[16] from saturated diamines while low-spin five- and six-coordinate cobalt(II) complexes have been characterized by Scheidt[17,18] and Glick and coworkers.[19,20]

In this paper, we report the successful extension of the Schiff base condensation reaction between *N,N'*-bis(2-aminoethyl)-1,3-propanediamine (2.3.2) and acetylacetone to cobalt(II) ions. Macrocyclic complexes containing both the diene (I) and dieno (II) forms of the 14-membered ligand have been isolated and characterized.

Various physical measurements, including a single crystal x-ray structure analysis of $[Co([14]dieneN_4)\cdot H_2O](PF_6)_2$, have confirmed the presence of both four- and five-coordinate, low-spin cobalt(II) in these new systems.[21]

Experimental Section

(A) Materials Used. *N,N'*-Bis(2-aminoethyl)-1,3-propanediamine (2.3.2) was used as received from Eastman Organic Chemicals, Rochester, N.Y. The 2,4-pentanedione (acac) was purchased from Aldrich Chemical Co., Milwaukee, Wis., and was used without further purification. Solvents employed in physical measurements were purchased commercially and were spectroquality grade. All other solvents and metal salts were reagent grade commercial materials.

All reactions in the synthesis of the cobalt(II) complexes were carried out under a nitrogen atmosphere using Kontes brand airless ware. 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 °C) BASF active copper catalyst, respectively.

All solutions used in physical measurements were prepared in a glove bag using solvents deaerated with nitrogen.

(B) General Synthetic Procedure. A 300-ml aqueous solution containing 7.47 g (0.03 mol) of cobalt acetate tetrahydrate was placed in a 500-ml round-bottom Schlenk flask, heated to boiling, and then deaerated with nitrogen until it cooled to room temperature. To this solution, a 4.8-g sample (0.03 mol) of deaerated 2.3.2 in 10 ml of water was added and the mixture was warmed and stirred under a nitrogen atmosphere for 15 min. Then, 6.01 g (0.06 mol) of deaerated acac in 10 ml of water was added and the resulting solution was refluxed for ~15 h under constant pressure of nitrogen. The solution changed from pink to a wine-red color which proved to be indicative of complex

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formation. Various derivatives were then prepared by the addition of sodium or ammonium salts of the desired anions.

12,14-Dimethyl-1,4,8,11-tetraazacyclotetradeca-11,13-dienecobalt(II) Hexafluorophosphate, [Co([14]dieneN$_4$)](PF$_6$)$_2$. An excess of ammonium hexafluorophosphate (15 g, 0.09 mol) in 50 ml of deaerated water was added to the hot reaction mixture and the resulting solution was allowed to cool to room temperature. It was then refrigerated overnight. The orange, needlelike crystals which formed were collected on a filter and dried for 48 h under vacuum on the Schlenk line. The filter containing the dried crystals was removed from the line while still sealed under nitrogen and transferred to a glove bag where the crystals were removed and placed into small bottles that were then sealed with paraffin and stored in a desiccator. When the crystals are dried at room temperature, the monoaquo complex, [Co([14]dieneN$_4$)·H$_2$O](PF$_6$)$_2$, is obtained; yield ~6 g. Anal. Calcd for $CoC_{12}H_{24}N_4P_2F_{12}$: C, 25.13; H, 4.22; N, 9.80; P, 10.72; F, 39.80; Co, 10.26. Found: C, 25.04; H, 4.04; N, 9.60; P, 10.66; F, 39.68; Co, 10.47.

12,14-Dimethyl-1,4,8,11-tetraazacyclotetradeca-11,13-dienecobalt(II) Iodide, [Co([14]dieneN$_4$]I$_2$. An iodide salt was prepared according to the procedure just described for the hexafluorophosphate derivative with the exception that the reaction mixture was concentrated to approximately 25 ml before an excess of sodium iodide (~15 g, 0.1 mol) was added. Reddish-black crystals formed when this solution was refrigerated overnight. The product was isolated by the procedure previously described, yield ~4 g. Anal. Calcd for $CoC_{12}H_{24}N_4I_2$: C, 26.84; H, 4.50; N, 10.43; I, 47.26; Co, 10.97. Found: C, 26.59; H, 4.55; N, 10.21; I, 47.35; Co, 11.05.

12,14-Dimethyl-1,4,8,11-tetraazacyclotetradeca-11,13-dienecobalt(II) Tetraisothiocyanatocobaltate(II), [Co([14]dieneN$_4$)][Co(NCS$_4$)]. The procedure described for the preparation of the hexafluorophosphate salt was followed with the exception that an excess of NaSCN (8 g, 0.1 mol) dissolved in 100 ml of deaerated water was added. The color of the solution immediately changed from a wine-red to a dark green color. Isolation of a dark green crystalline product was accomplished as previously described; yield ~10 g. Anal. Calcd for $Co_2C_{16}H_{24}N_8S_4$: C, 33.45; H, 4.21; N, 19.50; S, 22.33; Co, 20.51. Found: C, 33.42; H, 4.15; N, 19.75; S, 22.09; Co, 20.57.

12,14-Dimethyl-1,4,8,11-tetraazacyclotetradeca-11,13-dienatocobalt(II) Hexafluorophosphate, [Co([14]dienoN$_4$)]PF$_6$. A 4.0-g sample of [Co([14]dieneN$_4$)](PF$_6$)$_2$ was placed in a 250-ml round-bottom Schlenk flask which was then attached under a nitrogen atmosphere to the Schlenk line. Approximately 200 ml of a deaerated saturated solution of sodium hydroxide was then added to the flask. The resulting dark red solution was concentrated to ~100 ml and bright magenta crystals began to form. The mixture was refrigerated overnight and the crystals were then isolated as previously described; yield, ~3 g. Anal. Calcd for $CoC_{12}H_{23}N_4PF_6$: C, 33.74; H, 5.43; N, 13.11; P, 7.25; F, 26.68; Co, 13.79. Found: C, 33.75; H, 5.13; N, 13.05; P, 7.09; F, 26.94; Co, 13.71.

12,14-Dimethyl-1,4,8,11-tetraazacyclotetradeca-11,13-dienatocobalt(II) Iodide, [Co([14]dienoN$_4$)]I. The procedure used was that employed for the preparation of [Co([14]dienoN$_4$)]PF$_6$ with the exception that the iodide salt of the diene form of the macrocyclic complex was used as the starting material and the solution which resulted from the addition of the saturated NaOH solution was concentrated to ~25 ml. Upon concentration, dark maroon-red crystals formed. The crystals were isolated as described in the previous procedure; yield ~1.5 g. Samples of this derivative tended to decompose rapidly and gave irreproducible elemental analyses, although other physical data could be obtained.

(C) Physical Measurements. Elemental Analyses. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, on samples which had been dried in vacuo at 100 °C for at least 5 h.

Infrared Spectra. A Perkin-Elmer Model 457 infrared spectrophotometer was used to record the spectra using both the KBr pellet and Nujol mull techniques. Polystyrene was used as a standard to calibrate each spectrum.

Electronic Spectra. Visible and ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer. Solution spectra were run in matched 5.0-, 1.0-, and 0.1-cm quartz cells and solid state spectra were recorded using the diffuse transmittance technique.[22]

Conductivity Measurements. Conductivities were calculated from resistance measurements on 10^{-3} M solutions using a Yellow Springs Instruments Model 31 conductivity bridge. All solvents used to prepare solutions were deaerated with prepurified nitrogen. Solutions were prepared in a glove bag and the conductivity cell was kept in the glove bag during each measurement.

Magnetic Susceptibility Measurements. Magnetic susceptibilities of the complexes were measured using a Faraday apparatus. The susceptibilities of the ligands were calculated using Pascal's constants.[23] Values reported are averages of measurements made at field strengths of 7 and 5 kG. Inert atmosphere techniques were not used since the solids did not appear to be easily oxidized.

(D) Crystal Structure Determination of [Co([14]dieneN$_4$)·H$_2$O](PF$_6$)$_2$. Several crystals suitable for diffraction studies were chosen with the aid of a polarizing microscope. One of these with dimensions 0.23 × 0.24 × 0.37 mm was mounted on the end of a thin glass fiber with the long dimension approximately collinear with the fiber axis; the other crystals were saved for the density determination.

Preliminary precession photographs taken with Zr-filtered Mo Kα radiation (λ 0.7107 Å) showed the monoclinic Laue diffraction symmetry $2/m$ and displayed systematic absences consistent with space groups $C2/c$ or Cc.[24] The crystal and goniometer head were transferred to a computer controlled Picker FACS-1 diffractometer equipped with a Mo target tube and a Zr-foil filter. Accurate unit cell constants[26] were calculated by a least-squares treatment of the setting angles of 36 reflections, distributed in pairs between the $\pm 2\theta$ regions: $a = 22.482$ (3), $b = 16.741$ (2), $c = 15.572$ (2) Å, and $\beta = 131.59$ (2)° (λ 0.71069 Å). A Delauney reduction using these cell parameters confirmed the C centered monoclinic description. These cell constants led to a calculated density of 1.791 g/cm^3 at 20 ± 1 °C for the cell containing eight molecules; an experimental determination of the density, by the flotation method, was 1.786 (5) g/cm^3.

The intensity data were measured on the Picker diffractometer using the θ–2θ scan technique with Zr-filtered Mo Kα radiation and a take-off angle of ~2°. The range of each scan consisted of the estimated base width of 1.35° at $2\theta = 0°$ and an increment $\Delta(2\theta)° = (0.692) \tan \theta°$ to allow for α_1–α_2 dispersion; background was measured for 20 sec at the extremes of each scan. Brass attenuators were automatically inserted into the diffracted beam if the count rate exceeded ~9000 Hz. Three standard reflections well distributed in reciprocal space were monitored after every 100 data points. A gradual monotonic decrease (~7%) of the intensities, both individually and as a group, was observed during the course of data collection and was corrected for during the data reduction procedure. All independent, nonsystematically extinct data having $(\sin \theta)/\lambda \leq 0.649$ were thus measured.

With the cited crystal dimensions and a calculated linear absorption coefficient of 10.84 cm^{-1} for Mo Kα radiation, we estimate the largest error in a structure factor resulting from the neglect of absorption correction to be ~4% and no corrections were applied. The intensities after subtraction of background were directly reduced to a set of relative squared structure amplitudes, $|F_o|^2$, by the application of the standard Lorentz polarization factor (Lp) and a linear correction for the observed decrease in the intensities of the standards. Individual estimated standard deviations, based solely on counting statistics, for the reflections were calculated from

$$\sigma^2(|F_o|) = (C_t + k^2 B)/4|F_o|^2(Lp)^2$$

where C_t is the total count of the scan, k is the ratio of scanning time to total background counting time, and B is the total background count. All data having $|F_o| \leq 3\sigma(|F_o|)$ were taken to be unobserved and were not used in either the determination or refinement of the structure. Of the 5023 independent, nonsystematically extinct reflections measured, 3064 were retained for subsequent calculations.

The three dimensional Patterson map calculated using all independent data with $(\sin \theta)/\lambda \leq 0.52$ could be reasonably interpreted assuming the centric space group $C2/c$ and a set of trial coordinates that placed the cobalt and one phosphorus atom in general positions of the space group and randomly placing the remaining phosphorus atom at two locations on the twofold axis of the unit cell (4(e) positions).[24,25] Two cycles of full-matrix least-squares refinement[26] of the scale factor and positional parameters of these atoms resulted in a conventional R of 0.315. The function minimized was $\sum w(|F_o| - s|F_c|)^2$; wherein w is the weight assigned to each contributing reflection and s is the scale factor. In the initial refinements the weights were uniformly set equal to unity. The remaining portion of the structure was developed from a combination of difference syntheses and least-squares refinements. Three additional difference syntheses,

Table I. Atomic Coordinates in the Unit Cell[a]

Atom type	Coordinates		
	10^4x	10^4y	10^4z
Co	1692.5 (7)	1551.0 (7)	1879.7 (9)
N_1	1704 (4)	1695 (4)	671 (6)
N_2	2380 (5)	607 (4)	2319 (7)
N_3	1714 (5)	1396 (5)	3166 (7)
N_4	1037 (4)	2465 (4)	1473 (6)
C_1	2141 (7)	1047 (7)	628 (9)
C_2	2760 (7)	747 (6)	1827 (9)
C_3	3027 (7)	378 (8)	3565 (9)
C_4	2676 (7)	268 (7)	4120 (9)
C_5	2431 (6)	1050 (7)	4285 (8)
C_6	1505 (7)	2192 (7)	3355 (9)
C_7	818 (7)	2542 (7)	2190 (9)
C_8	740 (6)	2942 (5)	657 (8)
C_9	872 (7)	2903 (6)	−155 (9)
C_{10}	1345 (5)	2237 (6)	−110 (7)
C_{m1}	188 (7)	3636 (7)	392 (9)
C_{m2}	1339 (8)	2275 (8)	−1098 (9)
O_w	587 (4)	771 (4)	679 (6)
P_1	3354 (1)	3238 (1)	3466 (2)
F_1	3967 (6)	2819 (6)	3453 (8)
F_2	2949 (5)	2398 (4)	3262 (7)
F_3	3934 (6)	3078 (6)	4783 (6)
F_4	2734 (6)	3639 (6)	3478 (9)
F_5	2776 (5)	3350 (6)	2135 (6)
F_6	3733 (5)	4077 (4)	3638 (8)
P_2	0^b	−78 (2)	$^1/_4{}^b$
F_7	905 (4)	−81 (5)	3104 (8)
F_8	173 (6)	−742 (7)	3322 (8)
F_9	145 (7)	580 (8)	3296 (9)
P_3	0^b	5090 (2)	$^1/_4{}^b$
F_{10}	281 (6)	5113 (5)	3735 (7)
F_{11}	−630 (7)	4453 (7)	2096 (8)
F_{12}	−613 (6)	5764 (6)	2091 (9)

[a] The figure in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] The value of the coordinate is required by symmetry.

based on $F_o - F_c$, were required to locate the remaining carbon and heavier atoms.

Refinement of the model proceeded smoothly through several distinct phases. Initial refinements of the fully isotropic description utilized unit weights in a full-matrix least-squares procedure and converged to a value for R of 0.139. Empirical weights were then calculated as previously described[27] with the values for the coefficients of the power series being $a_0 = 2.86$, $a_1 = -5.49 \times 10^{-2}$, $a_2 = 9.05 \times 10^{-4}$, and $a_3 = -2.12 \times 10^{-6}$. A full anisotropic thermal description was then used for the remaining cycles of refinement. Limitations on computer core requirements necessitated the use of a block-diagonal, least-squares refinement. Several iterative cycles led to convergence for the conventional R factor of 0.0953 and a weighted R of 0.1083 and a final data/parameter ratio of 10.6. During the last cycle of refinement no parameter was shifted by more than 5% of its associated, estimated standard deviation. A final difference Fourier was judged to be free of significant features and had a maximum residual electron density of 0.4 e/Å^3.

Atomic coordinates and anisotropic thermal parameters for the 33 independent carbon and heavier atoms in the asymmetric unit are listed in Tables I and II along with the estimated standard deviation of each parameter as obtained from the last cycle of refinement. The successful refinement of the structure in $C2/c$ supports the initial choice of this centric space group.

Results and Discussion

Syntheses and Physical Properties. New macrocyclic cobalt(II) complexes have been prepared by the in situ condensation of 2.3.2 tetramine and acac in the presence of Co(II) ions. Complexes containing the 14-membered diene ligand, I, have been isolated from aqueous solutions at pH ~6, in the presence of PF_6^-, I^-, and $Co(NCS)_4^{2-}$ ions. Complexes containing PF_6^- and I^- counterions and the dieno ligand, II, have been prepared by deprotonation of the corresponding diene at pH ~10. Isolation of the dieno complex by addition of base and a counterion directly to the reaction mixture resulted in precipitation of unreacted Co(II) as the hydroxide and was generally avoided as a synthetic route to these complexes.

Although the general method of synthesis was the same for all derivatives reported in this study, differences in solubility of the various products required that slightly different procedures be used for their isolation. For example, both of the PF_6^- complexes and that containing the $Co(NCS)_4^{2-}$ anion are relatively insoluble and began to crystallize from the reaction solutions immediately upon addition of the counterion. Crystals obtained from these dilute solutions are generally well-formed and analytically pure. The complex, $[Co([14]dieneN_4)\cdot H_2O](PF_6)_2$, is isolated initially as the monohydrate (vide infra) which can be dehydrated by heating the complex for 24 h in vacuo at 100 °C. Upon drying, the translucent brownish-orange crystals turn opaque. All of the other derivatives crystallize from solution in anhydrous form. In order to isolate the I^- derivatives, it was necessary to concentrate the reaction solutions nearly to dryness. As a result, the products obtained were not highly crystalline and were difficult to purify. All samples had to be dried rigorously to retard decomposition (presumably oxidation) in the solid state. Once thoroughly dried, solid samples of the PF_6^- and $Co(NCS)_4^{2-}$ derivatives of ligand I are stable in air for several months. Both I^- derivatives and the PF_6^- complex of ligand II oxidize more rapidly in air and the samples must be stored under nitrogen. All of the complexes are fairly soluble in water and the lower alcohols and much less soluble in DMF, DMSO, and CH_3NO_2. All of the new compounds are susceptible to rapid air oxidation in solutions at room temperature.

Characterization. The five new complexes reported in this study have been characterized on the basis of results of elemental analyses, conductivity and magnetic susceptibility measurements, and visible, uv, and ir spectra. In addition, a single crystal structure determination has been made of $[Co([14]dieneN_4)H_2O](PF_6)_2$.

Physical data for the new complexes are summarized in Table III. The most convincing proof for formation of the macrocyclic ligands is obtained from the infrared spectra of the various derivatives. Evidence for cyclization is demonstrated by the absence of absorption bands that can be attributed to either free or coordinated NH_2 or $>C{=}O$ modes and the presence of bands assignable to $C{=}N$ (diene) or $C\overset{\dots}{=}N$, $C\overset{\dots}{=}C$ (dieno) stretching vibrations. The absence of an absorption at ~1650 cm^{-1} for the dieno complexes indicates that delocalization of the imine π electrons has occurred following deprotonation at the γ carbon. Spectra of the $[Co([14]dieneN_4)]^{2+}$ and $[Co([14]dienoN_4)]^+$ derivatives are very similar to spectra of the corresponding Ni(II) and Cu(II) complexes which have been previously reported.[4] Other ir bands which are observed in the spectra include one which is attributed to the NH stretching vibration. In the PF_6^- derivatives this is found as a sharp, relatively strong band at ~3270 cm^{-1}; whereas in spectra of the other derivatives it is broader and shifted to lower energies suggesting some hydrogen bonding with the anions.[28] Bands attributable to the PF_6^- anions are not split but occur as two strong, sharp absorptions at ~840 and 565 cm^{-1}. These data suggest that the PF_6^- anions are not coordinated[29] and that the complexes contain square-planar cobalt(II), a conclusion which is fully consistent with interpretation of the electronic spectra and which may be inferred from results of the crystal structure determination of the five-coordinate monoaquo complex.

The ir spectrum of $[Co([14]dieneN_4)\cdot H_2O](PF_6)_2$ also includes strong, sharp peaks at 3650, 3580, and 1630 cm^{-1} that are assigned to the asymmetric and symmetric stretching vibrations and symmetric bending mode of coordinated water.

Table II. Thermal Parameters[a]

Atom type	Anisotropic parameters, Å^2					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	2.82 (4)	2.67 (4)	2.71 (4)	−0.23 (4)	1.79 (4)	−0.37 (4)
N_1	3.7 (3)	3.1 (3)	2.6 (3)	0.2 (3)	2.0 (3)	−0.1 (2)
N_2	3.8 (4)	3.2 (3)	4.3 (4)	0.7 (3)	2.8 (3)	0.3 (3)
N_3	4.0 (4)	3.6 (4)	3.7 (3)	0.5 (3)	2.7 (3)	0.4 (3)
N_4	3.4 (3)	2.6 (3)	3.9 (3)	0.2 (2)	2.6 (3)	−0.1 (3)
C_1	7.0 (7)	5.1 (6)	5.5 (6)	1.6 (5)	5.1 (6)	0.4 (4)
C_2	4.9 (5)	4.4 (5)	6.2 (6)	1.0 (4)	4.0 (5)	0.4 (4)
C_3	3.6 (5)	6.9 (7)	4.8 (6)	0.6 (5)	2.1 (4)	1.0 (5)
C_4	4.5 (5)	5.3 (6)	4.9 (5)	0.8 (4)	2.7 (5)	1.7 (4)
C_5	4.3 (5)	6.2 (6)	2.9 (4)	−0.7 (5)	1.8 (4)	−0.6 (4)
C_6	6.2 (6)	4.8 (5)	4.9 (5)	−0.5 (5)	4.4 (5)	−0.5 (4)
C_7	6.6 (7)	4.4 (5)	5.9 (6)	1.6 (5)	5.1 (6)	0.5 (4)
C_8	3.8 (4)	2.8 (4)	4.5 (5)	0.1 (3)	2.7 (4)	−0.2 (3)
C_9	5.5 (6)	4.2 (5)	4.2 (5)	0.8 (4)	3.4 (5)	1.0 (4)
C_{10}	3.7 (4)	4.1 (4)	2.7 (4)	−1.0 (3)	2.2 (3)	−1.1 (3)
C_{m1}	6.1 (6)	4.0 (5)	6.4 (6)	1.9 (5)	4.0 (6)	1.0 (4)
C_{m2}	7.1 (7)	7.1 (7)	3.9 (5)	−1.6 (6)	4.0 (5)	−0.6 (5)
O_w	3.5 (3)	3.9 (3)	4.9 (3)	−1.0 (2)	2.3 (3)	−1.0 (3)
P_1	3.6 (1)	3.1 (1)	3.9 (1)	−0.53 (8)	2.35 (9)	−0.23 (8)
F_1	9.7 (6)	11.0 (6)	10.7 (6)	4.4 (5)	8.3 (5)	3.3 (5)
F_2	6.9 (4)	5.2 (4)	9.4 (5)	−2.1 (3)	4.5 (4)	−0.6 (3)
F_3	9.8 (6)	9.6 (6)	4.2 (3)	0.2 (4)	3.3 (4)	0.0 (4)
F_4	10.6 (6)	8.6 (5)	13.8 (7)	2.2 (5)	10.0 (6)	0.0 (5)
F_5	8.0 (5)	10.2 (6)	4.7 (3)	−0.2 (4)	3.1 (4)	0.6 (4)
F_6	7.8 (5)	4.8 (4)	11.7 (6)	−2.3 (3)	4.4 (5)	0.5 (4)
P_2	3.7 (2)	4.7 (2)	4.2 (2)	0[b]	2.9 (1)	0[b]
F_7	4.7 (3)	8.2 (5)	11.2 (6)	−0.2 (3)	4.8 (4)	1.8 (4)
F_8	8.5 (6)	14.9 (8)	10.1 (6)	−0.2 (5)	6.0 (5)	5.4 (6)
F_9	11.7 (8)	15.5 (9)	18.9 (9)	−5.8 (7)	10.4 (9)	−12.2 (9)
P_3	4.9 (2)	4.0 (2)	4.1 (2)	0[b]	2.7 (2)	0[b]
F_{10}	11.5 (6)	8.6 (5)	6.2 (4)	−0.2 (5)	5.8 (5)	−0.1 (4)
F_{11}	13.9 (8)	12.3 (8)	8.7 (6)	−8.9 (7)	3.9 (6)	0.8 (5)
F_{12}	11.7 (7)	11.0 (7)	13.3 (8)	6.4 (6)	9.3 (7)	4.8 (6)

[a] The number in parentheses is the estimated standard deviation in the last significant figure. [b] Required by symmetry.

Table III. Physical Data for Macrocyclic Cobalt(II) Complexes

Complex	Color	Selected ir bands, cm^{-1} [a]		Λ_M, mhos cm^2/mol[b]			μ_{eff}, μ_B[c]
		$\nu_{C=N}$	$\nu_{C\overset{...}{=}N, C\overset{...}{=}C}$	H_2O	MeOH	CH_3NO_2	
$[Co([14]dieneN_4)\cdot H_2O](PF_6)_2$	Orange	1680		210	180		2.05 ± 0.05
$[Co([14]dieneN_4)]I_2$	Maroon	1645		248	140		1.88 ± 0.04
$[Co([14]dieneN_4)][Co(NCS)_4]$	Green	1668		302	95	98	3.21 ± 0.10[d]
$[Co([14]dienoN_4)]PF_6$	Magenta		1550, 1538	110	70		2.33 ± 0.04
$[Co([14]dienoN_4)]I$	Brown		1580, 1530	150	78		1.94 ± 0.04

[a] Nujol mulls. [b] Concentrations of ~1 × 10^{-3} M; typical values of 1:1 electrolytes are 90–150 (H_2O), 60–110 (MeOH), 80-100 (CH_3NO_2); typical values of 2:1 electrolytes are 200–250 (H_2O), 130–160 (MeOH), 150–200 (CH_3NO_2). [c] Pascal's constants were used to determine diamagnetic corrections. [d] Value reported is average μ_{eff}/Co.

In contrast to the anhydrous form of this complex, the absorption band attributed to the NH stretching mode has been split into a doublet with peaks at 3260 and 3290 cm^{-1} in the aquo complex. A possible cause for this will be discussed later.

Results of conductivity measurements (Table III) in water and methanol are consistent with formulation of the simple diene complexes as 2:1 electrolytes and the dieno complexes as 1:1 electrolytes.[30] The $Co(NCS)_4^{2-}$ derivative exhibits 2:2 electrolyte behavior in methanol and nitromethane; however, the value of the molar conductance in aqueous solution (Λ_M = 302) is too high for 2:2 and suggests that partial dissociation of the complex anion occurs.[30] This observation is consistent with visible spectral data of the $Co(NCS)_4^{2-}$ derivative obtained in aqueous solution which show no bands indicative of tetrahedral cobalt(II).

Magnetic moments of the PF_6^- and I^- complexes (Table III) fall in the range μ_{eff} = 1.88–2.33 μ_B and indicate an $S = {}^1/_2$ spin state for the cobalt(II) ion. More complicated magnetic behavior is observed for the $Co(NCS)_4^{2-}$ complex since it contains two cobalt ions, one presumably with $S = {}^3/_2$ (T_d) and one with $S = {}^1/_2$ (square planar). The average value of μ_{eff} is calculated as 3.21 μ_B. In order to determine the susceptibility of the cation alone, a correction for the tetrahedral anion must be made. Generally, magnetic moments of tetrahedral cobalt, $S = {}^3/_2$, show some orbital contribution although not as much as that observed for $S = {}^3/_2$ octahedral. Typical values of μ_{eff} are 4.4–4.8 μ_B, with the lower values being expected for stronger field ligands.[31,32] Using the formula $\mu_{eff} = \mu_{s.o.}(1 - [\alpha\lambda/\Delta])$, where $\alpha = 4$, $\lambda = -172$, and Δ = 7800 cm^{-1} (obtained from the visible spectrum), the calculated μ_{eff} for $Co(NCS)_4^{2-}$ in this complex is 4.21 μ_B (χ_M = 7553 × 10^{-6}). When this value is subtracted from the total corrected susceptibility of the complex, μ_{eff} for the cation is 1.64 μ_B. This value is slightly lower than the others reported in Table III. If one allows that the orbital contribution to the susceptibility of the tetrahedral Co(II) anion might be further quenched with χ_M = 7100 × 10^{-6} (μ_{eff} = 4.1 μ_B), a μ_{eff} of 1.92 μ_B for the cation is obtained. This value is close to that expected for low-spin Co(II). Although the results from the magnetic data alone are therefore somewhat ambiguous, when the magnetic data are taken in conjunction with the other physical data obtained for this complex, presence of the

Table IV. Electronic Spectra of the Macrocyclic Cobalt(II) Complexes

	Absorption bands										
	Methanol			Solid state		Water			Nitromethane		
	λ_{max}			λ_{max}		λ_{max}			λ_{max}		
Compd	nm	kK	ϵ	nm	kK	nm	kK	ϵ	nm	kK	ϵ
$[Co([14]dieneN_4)](PF_6)_2$				1600	6.2						
				1422	7.0 sh						
	635	15.7	76			650	15.4	29			
	520	19.2	165			540	18.5	447			
				461	21.7 sh	450	22.2	777			
				410	24.4 sh						
	375	26.7	980 sh	400	25.0	415	24.1	1214			
	290	34.5	2 718 sh	380	26.3	315	31.7	2780			
	215	46.5	15 436								
$[Co([14]dieneN_4)]I_2$				2070	4.8						
				1713	5.8						
						1290	7.7	17.2			
						1149	8.7	16.6			
						961	10.4	21.5			
				540	18.5						
	482	20.7	301	480	20.8						
	352	28.4	2 476	350	28.6	370	27.0	1675			
	285	35.1	3 029	294	34.0						
$[Co([14]dieneN_4)][Co(NCS)_4]$				1300	7.7				1245	8.0	(70)
						660	15.2	190			
				625	16.0				618	16.2	(1180)
				590	16.9 sh				582	17.2	(1090)
									567	17.6	(1090)
	510	19.6	410			515	19.4	224	530	18.9	(1113)
	462	21.6	1 450	460	21.7						
	440	22.7	1 370	430	23.3						
	370	27.0	2 000			370	27.0	2355 sh	380	26.3	(2500)
	284	35.2	4 600			312	32.2	1900 sh	342	29.2	(5600)
				214	46.7						
$[Co([14]dienoN_4)]PF_6$				1140	8.8						
						960	10.4	265			
	542	18.5	128	543	18.4	535	18.7	270			
	415	24.1	350 sh			405	24.6	810			
	360	27.8	11 140			365	27.4	3100			
	350	28.6	8 600 sh	330	30.3	338	29.6	4100			
	280	35.7	20 000 sh								
	256	39.1	73 000								
$[Co([14]dienoN_4)]I$				1720	5.8						
				1535	6.5						
				580	17.2						
	480	20.8	800	440	22.7						
	370	27.0	920								
	350	28.6	2 500	330	30.3						
	285	35.1	3 100	235	42.5						
				215	46.5						
	220	45.4	14 700								

low-spin Co(II) cation is indicated.

Visible and ultraviolet spectra of the Co(II) complexes were obtained both in solution and in the solid state (diffuse transmittance). These results are summarized in Table IV. While no specific band assignments can be made, several generalizations are applicable. First, bands at energies greater than 34 000 cm^{-1} are attributed to charge transfer transitions, while d–d bands are observed in the range 4 800–33 000 cm^{-1}. Spectra of the crystalline complexes suspended in Nujol mulls are different from those obtained in solution. In general, the solid state spectra of the simple 1:1 and 2:1 type complexes include low-energy bands in the 4800–8800 cm^{-1} region. Such low-energy absorptions are now accepted as typical of square-planar cobalt(II).[33-36] Bands in the ranges 17 000–22 000 and 24 000–31 000 cm^{-1} are also observed. In aqueous and methanolic solutions, new absorptions at ~16 000 and 19 000 cm^{-1} appear. Such bands are characteristic of octahedral Co(II) and suggest coordination of the solvent. It should be noted that bands in the spectra of the dieno complexes in general occur at higher energies than those in the diene complexes. This indicates that the uninegative macrocyclic ligand, with partial delocalization of π electrons, produces a stronger ligand field than the β-diimine ligand.

Spectra of $[Co([14]dieneN_4)][Co(NCS)_4]$ in the solid state show absorptions at ~7 800, ~16 000, and ~17 000 cm^{-1} which are typical of the tetrahedral $Co(NCS)_4^{2-}$ ion.[31,32] Disappearance of these bands in aqueous solution and the appearance of new bands at 15 200 and 19 400 cm^{-1} confirms dissociation of the anion and formation of the hydrated macrocyclic Co(II) cation.

The stereochemistry of the new complexes has been investigated further by x-ray methods. Results obtained from the single crystal structure determination of the $[Co([14]dieneN_4)H_2O](PF_6)_2$ derivative fully support the conclusions drawn from the other physical measurements and also reveal that the hexafluorophosphate anion may be weakly coordinated to the Co(II) ion of the macrocyclic cation.

Figure 1 is a computer-drawn model of the cation as it exists in the monoclinic crystal.[25] Each atom is represented by an ellipsoid having the relative size and orientation required by the thermal parameters presented in Table II. In addition to being complexed by the four nitrogen atoms of the macrocyclic ligand, the water molecule is also bonded to the cobalt(II) ion. Important bond distances and angles for the macrocyclic cation

Table V. Bond Lengths within the Cationic Macrocycle[a]

Type	Length, Å	Type	Length, Å
$Co-N_1$	1.914 (7)	N_2-C_2	1.497 (9)
$Co-N_4$	1.917 (7)	N_2-C_3	1.509 (8)
$Co-N_2$	1.987 (7)	N_3-C_5	1.498 (9)
$Co-N_3$	1.989 (7)	N_3-C_6	1.503 (9)
N_1-C_1	1.494 (9)	C_1-C_2	1.491 (8)
N_4-C_7	1.497 (9)	C_3-C_4	1.518 (10)
N_1-C_{10}	1.285 (9)	C_4-C_5	1.506 (9)
N_4-C_8	1.265 (9)		
C_8-C_9	1.489 (9)	C_6-C_7	1.517 (8)
C_9-C_{10}	1.510 (9)	$Co-O_w$	2.283 (9)
C_8-C_{m1}	1.542 (9)		
$C_{10}-C_{m2}$	1.531 (9)	$Co-F_2$	2.559 (10)

[a] The number in parentheses following each datum is the estimated standard deviation in the last significant digit.

Table VI. Bond Angles within the Cationic Macrocycle[a]

N_1CoN_4	94.8 (3)	$N_1C_1C_2$	106.5 (9)	$C_9C_{10}N_1$	123.1 (1.1)
N_1CoN_2	85.6 (3)	$C_1C_2N_2$	108.6 (9)	$C_{10}N_1C_1$	119.2 (9)
N_2CoN_3	93.2 (3)	$C_2N_2C_3$	108.0 (9)	$N_4C_8C_{m1}$	123.0 (1.1)
N_3CoN_4	86.4 (3)	$N_2C_3C_4$	110.0 (8)	$C_{m1}C_8C_9$	112.8 (1.0)
CoN_1C_1	113.0 (3)	$C_3C_4C_5$	112.3 (9)	$N_1C_{10}C_{m2}$	124.2 (1.2)
CoN_1C_{10}	127.5 (4)	$C_4C_5N_3$	111.8 (8)	$C_{m2}C_{10}C_9$	112.8 (9)
CoN_4C_7	112.6 (5)	$C_5N_3C_6$	110.5 (8)	O_wCoN_1	89.1 (6)
CoN_4C_8	126.4 (4)	$N_3C_6C_7$	108.1 (9)	O_wCoN_2	90.1 (5)
CoN_2C_2	106.1 (5)	$C_6C_7N_4$	106.3 (9)	O_wCoN_3	92.0 (6)
CoN_2C_3	120.7 (4)	$C_7N_4C_8$	118.8 (9)	O_wCoN_4	90.3 (5)
CoN_3C_5	120.5 (4)	$N_4C_8C_9$	124.2 (10)	F_2CoN_1	91.7 (3)
CoN_3C_6	106.2 (4)	$C_8C_9C_{10}$	121.9 (7)	F_2CoN_2	88.8 (3)
				F_2CoN_3	87.1 (3)
				F_2CoN_4	90.7 (3)

[a] Numbers in parentheses following each datum are the estimated standard deviations in the last significant figure.

Table VII. Bond Lengths within the[a] Hexafluorophosphate Anions

Type	Length, Å	Type	Length, Å
P_1-F_1	1.558 (8)	P_2-F_7	1.578 (9)
P_1-F_2	1.588 (7)	P_2-F_8	1.533 (9)
P_1-F_3	1.559 (8)	P_2-F_9	1.554 (8)
P_1-F_4	1.559 (8)	P_3-F_{10}	1.577 (9)
P_1-F_5	1.563 (8)	P_3-F_{11}	1.538 (8)
P_1-F_6	1.571 (7)	P_3-F_{12}	1.524 (9)

[a] The numbers in parentheses are the estimated standard deviations in the last significant figure.

and the hexafluorophosphate anions are presented in Tables V–VIII.

Although not required by the crystalline arrangement, the macrocyclic cation exhibits nearly exact C_s-*m* symmetry. The pseudomirror plane contains the Co(II) ion, carbon atoms C_4 and C_9, and the oxygen atom, O_w, of the coordinated water molecule; the average deviation of these atoms from the best plane through them is only 0.002 Å. Departures from exact mirror symmetry are trivial and the overall configuration of the cationic complex is consistent with ideal cis-meso symmetry.[37] In addition to being cis with respect to each other, the amine hydrogen atoms are also cis relative to the coordinated water molecule.

Using N_i and N_a to differentiate between the imine and amine type nitrogen atoms and C_a to denote the aliphatic carbon atoms of the polyamine backbone, averaged lengths of chemically analogous bonds are $Co-N_i = 1.915$, $Co-N_a = 1.988$, $N_a-C_a = 1.501$, $N_i-C = 1.496$, and $C_a-C_a = 1.508$ Å. The difference in lengths between the two distinct classes of Co–N bonds is attributable to the difference in radius of a trigonally sp^2-hybridized nitrogen as compared to a tetrahedrally sp^3-hybridized nitrogen atom. A similar nonequivalence in bond lengths has been observed in several closely related macrocyclic systems that contain both coordinated imine and amine type nitrogen atoms and may be considered a regular structural feature in complexes of this type.[19,20,27,38] The two Co–N bonding distances observed in the present structure are in agreement with values determined in other low-spin Co(II) macrocyclic complexes by Glick et al.[19,20]

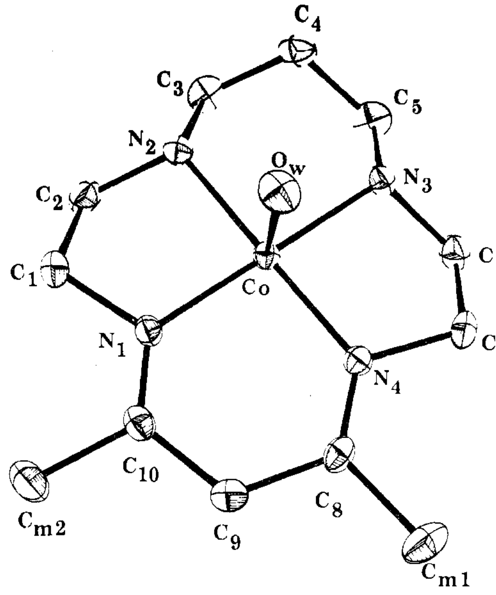

Figure 1. Computer-drawn model of the macrocyclic $[Co([14]\text{-}dieneN_4)\cdot H_2O]^{2+}$ cation.

Table VIII. Bond Angles within the Hexafluorophosphate Anions

Type	Angle, deg	Type	Angle, deg
$F_1P_1F_2$	89.7 (6)	$F_4P_1F_5$	90.0 (6)
$F_1P_1F_3$	88.1 (5)	$F_4P_1F_6$	90.0 (6)
$F_1P_1F_5$	90.1 (5)	$F_5P_1F_6$	89.9 (5)
$F_1P_1F_6$	91.1 (6)	$F_7P_2F_8$	91.7 (5)
$F_2P_1F_3$	88.8 (5)	$F_7P_2F_9$	90.6 (4)
$F_2P_1F_4$	89.2 (5)	$F_8P_2F_9$	90.6 (7)
$F_2P_1F_5$	88.8 (5)	$F_{10}P_3F_{11}$	89.3 (5)
$F_3P_1F_4$	91.8 (6)	$F_{10}P_3F_{12}$	91.3 (7)
$F_3P_1F_6$	92.5 (5)	$F_{11}P_3F_{13}$	92.6 (5)

Within the β-diketonate residue that has been protonated at the γ carbon atom, C_9, the average bond lengths reflect a localization of the π electrons to give a β-diimine linkage: $N_i{=}C = 1.275$; $C-C = 1.500$; and $C_m-C = 1.537$ Å. Both the bonding distances and angles displayed in the macrocyclic ligand indicate that little, if any, delocalization of the π electrons extends outside the two C═N bonds. The C_8-N_4 and $C_{10}-N_1$ bond distances are within the range expected for a fully localized C═N bond.

The Co(II) ion is fully five coordinate and effectively six coordinate in the solid state. In addition to being complexed by the four nitrogen atoms of the macrocyclic ligand, the oxygen atom, O_w, of the water molecule is bonded at a distance of 2.283 (9) Å. Similar Co–O bonding distances have been observed in other Co(II)–aquo complexes.[39,40] The four O_w-Co-N angles average to 90.4 (8)°. On the opposite side of the macrocycle at a distance of 2.559 (10) Å from the Co(II) ion is a fluorine atom, F_2, of the PF_6^- ion that occupies the general position in the unit cell. The four F–Co–N angles average to 89.6 (1.6)° and the O_w-Co-F angle is 178.6 (4)°. The fluorine atom resides in a position consistent with distorted octahedral geometry. Figure 2 depicts the arrangement of this PF_6^- ion with respect to the macrocyclic complex.

The four nitrogen atoms of the macrocyclic ligand are virtually coplanar and have an average deviation from exact planarity of 0.005 Å. The Co(II) ion is displaced from this plane (by 0.015 Å) toward the coordinated water molecule. In studies of low-spin Co(II) porphyrins, Scheidt[17,18] has

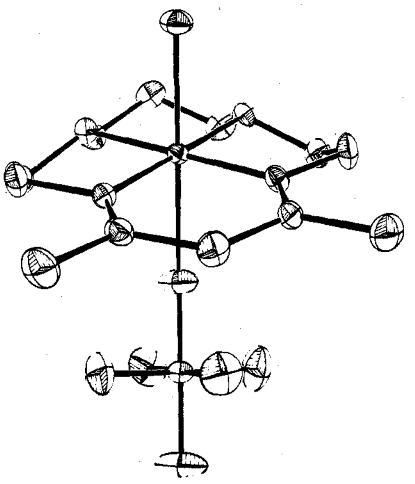

Figure 2. Location of PF$_6^-$ anion with respect to the macrocyclic cation.

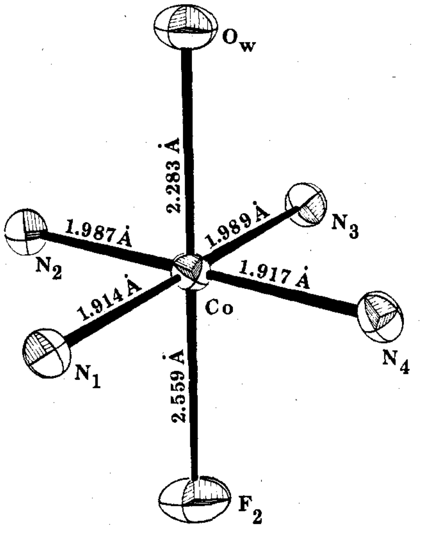

Figure 3. Bond distances obtained for the CoN$_4$OF coordination group.

observed a 0.14-Å displacement of the Co(II) ion toward the apical ligand in a five-coordinate species, while in a six-coordinate complex the metal atom resides in the plane. Glick et al.[19,20] have also reported an exact positioning of the low-spin Co(II) ion in the mean plane of the four nitrogen atoms in their studies on six-coordinate, macrocyclic complexes. Since in the present case the displacement is trivial, it may be concluded that the PF$_6^-$ group is exerting some influence on the metal ion causing it to be more nearly positioned in the mean plane of the N$_4$ girdle. The observed Co–F distance is ~0.5 Å longer than that observed in CoF$_2$ (2.10 Å) and is indicative of a weak interaction. The lack of any observed splittings of the bands assigned to absorptions of the PF$_6^-$ ions in the infrared spectrum, the conductivity data, and the solid state magnetic moment and visible spectrum are also consistent with a weak interaction.

The CoN$_4$OF coordination group is displayed in Figure 3. The average O–N distance of 3.01 Å is greater than the sum of the van der Waals' radii (2.90 Å) of an oxygen and a nitrogen atom.[41] Placement of the hydrogen atoms at the expected positions on the amine nitrogen atoms reveals that the resulting H$_2$O---H separation is ~2.6 Å. This distance is virtually equal to the sum of the van der Waals' radii for these two types of atoms and may indicate that hydrogen bonding is occurring. This would explain in part the cis configuration of the amine hydrogen atoms with respect to the water molecule.

As cited earlier, the infrared spectrum of [Co([14]dieneN$_4$)·H$_2$O](PF$_6$)$_2$ includes distinct bands at 3290 and 3260 cm^{-1} that are assigned to the N–H stretching mode. This doublet character is not observed in the spectrum of the anhydrous complex; rather a sharp band at 3270 cm^{-1} with a weak shoulder at 3290 cm^{-1} is detected. Based on the results of the crystal structure determination, only one absorption band in the spectrum of the monoaquo complex would be expected due to the near equivalency of the two >N–H groups. If, however, the conformation in which the amine hydrogen atoms are trans with respect to each other is also present as a five-coordinate, monoaquo complex, then hydrogen bonding would render the >N–H groups nonequivalent and two absorption bonds would be expected. Both cis and trans isomers have been detected by Elfring and Rose[42,43] in a solution NMR study of the related 13-membered macrocyclic complex [Ni([13]dieneN$_4$)](PF$_6$)$_2$. It is not unreasonable to expect a similar situation to exist in the present case. Dehydration of a mixture of the possible isomers of the monoaquo complex might then result in >N–H groups that are nearly equivalent and may not be easily differentiated by infrared methods. In the process of selecting a crystal for structural studies, a crystal of the cis-meso isomer may have been arbitrarily chosen from a sample containing crystals of the other possible isomers.

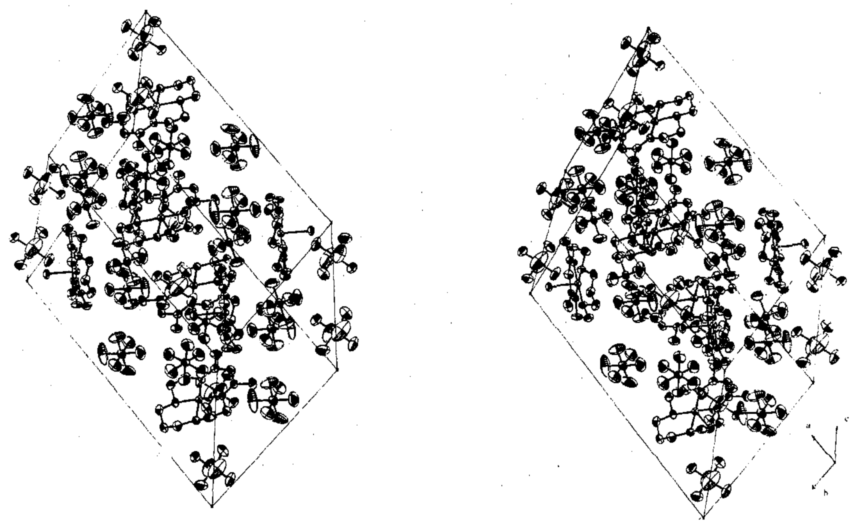

Figure 4. Stereoscopic view of the molecular packing in the crystalline complex.

The more stringent steric requirement of a five- relative to a six-membered ring is reflected in the ~0.2 Å difference between the N–N separations in the two types of rings. The five-membered ring containing N_1 and N_2 has a δ configuration; carbon atom C_1 is 0.09 Å below the CoN_1N_2 plane while carbon atom C_2 is 0.55 Å above this plane. The five-membered ring containing N_3 and N_4 also has a δ configuration; C_6 is 0.51 Å above the plane formed by CoN_3N_4 and C_7 is 0.14 Å below this plane. The six-membered fully saturated ring has the chair conformation in which carbon atom C_4 is displaced 0.75 Å below the best plane through the atoms N_2, N_3, C_3, C_5, while the cobalt atom is displaced 0.64 Å above this plane.

For the acetylacetone residue, local coplanarity is preserved within the groups N_4, C_8, C_9, C_{m1} and N_1, C_{10}, C_9, C_{m2}. The mean deviation from exact planarity does not exceed 0.002 Å in either case, and the dihedral angle between the two mean planes is only 5°. For the five-atom group N_1, N_2, C_8, C_9, C_{10} the average displacement of an atom from the best plane through them is only 0.014 Å. Relative to $[Ni([13]\text{-}dienoN_4)]ClO_4$,[38] the C_8–C_9–C_{10} angle has been reduced by ~6° upon protonation but is still ~13° greater than the ideal tetrahedral angle. In *trans*-dibromobis(acetylacetone)nickel(II), a complex containing coordinated ketonic molecules of acetylacetone, the internal angle at the γ carbon atom is 114° but is accompanied by a large displacement of the γ carbon atom resulting in a nonplanar ring.[44] In the present case, only a 0.05-Å displacement of C_9 from the best plane through atoms N_1, N_4, C_8, C_{10} is observed. Apparently, the rigid nature of the macrocyclic ligand prevents C_9 from being significantly displaced from the mean plane of the acetylacetone residue and the C_8–C_9–C_{10} angle cannot be further reduced.

Figure 4 is a stereoscopic view of the molecular packing. The arrangement consists of the macrocyclic cation, the water molecule, and a PF_6^- anion all occupying general positions and a PF_6^- anion randomly distributed between two independent sites in 4(e) special positions of the C centered monoclinic cell. The macrocyclic complexes form sheets that are perpendicular to and positioned approximately $^1/_4$ and $^3/_4$ along the *a* axis. Separating these sheets are layers of the disordered PF_6^- anions. The phosphorus atoms of the disordered anions lie on the 100 and 200 crystallographic planes. Within each layer the PF_6^- ions form independent, nearly linear chains. Both chains are perpendicular to the *b* axis and parallel to the *c* axis and each has an occupancy factor of 0.5. No short intermolecular contact distances are observed in the crystalline complex. Thus the packing of the disordered PF_6^- groups is relatively open and may account for a slightly higher than usual *R* factor.

In an earlier paper,[4] we attributed differences in relative acidity of the coordinated 13-, 14-, and 15-membered ligands to steric crowding and/or strain at the γ carbon which were expected to be a function of ring size. A comparison of the structural data now available on the 13- and 14-membered systems suggests that such steric effects may not be as important as previously assumed and that electronic effects due to the configuration of the metal ion may be more important.

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Registry No. $[Co([14]dieneN_4)\cdot H_2O](PF_6)_2$, 59982-25-1; $[Co([14]dieneN_4)]I_2$, 59982-33-1; $[Co([14]dieneN_4)][Co(NCS)_4]$, 59982-31-9; $[Co([14]dienoN_4)]PF_6$, 59982-28-4; $[Co([14]dienoN_4)]I$, 59982-29-5; $[Co([14]dieneN_4)](PF_6)_2$, 59982-32-0; acac, 123-54-6; *N,N'*-bis(2-aminoethyl)-1,3-propanediamine, 4741-99-5.

Supplementary Material Available: A listing of structure factor amplitudes for $[Co([14]dieneN_4)\cdot H_2O](PF_6)_2$ (14 pages). Ordering information is given on any current masthead page.

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