tributing to $(\lambda_i)_j$ are expected to be mostly enthalpic. If we then consider

$$\Delta H^{\ddagger}{}_{13} = \frac{(\Delta H^{\ddagger}{}_{11} + \delta H^{\ddagger}{}_{33})}{2}(1 - 4[\alpha']^2) + \frac{\Delta H^{\circ}{}_{13}}{2}(1 + 4\alpha')$$

then $\Delta H^{\ddagger}{}_{12} - \Delta H^{\ddagger}{}_{13} \simeq (\Delta H^{\ddagger}{}_{22} - \Delta H^{\ddagger}{}_{33})/2$, since $(\alpha - \alpha')$ and $(\alpha^2 - [\alpha']^2)$ are very small ($\sim 10^{-3}$). We further expect that $\Delta(\Delta H^{\ddagger}{}_{12}) = \Delta H^{\ddagger}{}_{12} - \Delta H^{\ddagger}{}_{13} \simeq [(\lambda_i)_2 - (\lambda_i)_3]/8$ since $(\lambda_o)_2 \simeq (\lambda_o)_3$ (the macrocyclic complexes are about the same size and have the same charge).

(64) R. A. Marcus and N. Sutin, *Inorg. Chem.*, **14**, 213 (1975).

(65) Note that for the inner-sphere reactions the $Co^{II}-OH_2$ "bond energies" ($\Delta G^{\circ}{}_{A_2}$ and $\Delta G^{\circ}{}_{B_2}$) in Scheme II may not be identical and their difference may contribute to $\Delta(\Delta H^{\ddagger}{}_{12})$.

(66) In addition to the examples cited here, we have found $\Delta H^{\ddagger} = 49$ kJ mol^{-1} for the Co([14]dieneN$_4$-one)(OH$_2$)$_2^{3+}$/Co([14]tetraeneN$_4$)(OH$_2$)$_2^{2+}$ "exchange" reaction (R. Sriram and J. F. Endicott, unpublished observations), in contrast to the values of $\Delta H^{\ddagger} \simeq 25$ kJ mol^{-1} found for the inner-sphere "exchange" reactions in Table V. This is very nicely consistent with Figure 3 and the conclusion that $\Delta G_i(IS) = 0.5\Delta G_i(OS)$, and once again indicates that the similar ratios of self-exchange rates for outer-sphere and inner-sphere pathways of the [14]tetraeneN$_4$ and [14]dieneN$_4$ systems indicate a relatively large entropic contribution in the inner-sphere reactions of the [14]dieneN$_4$ complexes.

(67) For the first acid hydrolysis steps of Co([14]dieneN$_4$)Cl$_2^+$ and Co([14]tetraene N$_4$)Cl$_2^+$, $\Delta S^{\ddagger} = +51$[18d] and -24 kJ mol^{-1} deg^{-1},[22] respectively. This difference has been attributed to "relaxation of strain" in a dissociative transition state. Similar arguments have been proposed for hydrolyses in a variety of macrocyclic complexes; various aspects of this question have been discussed in ref 12, 18d, 68, and 69. Macrocyclic complexes with asymmetric axial ligation do not consistently exhibit variations in $\Delta S^{\ddagger}$, perhaps owing to differences in stability of isomeric species. However, homolyses of Co([14]diene N$_4$)OH$_2$X^{2+} complexes have strongly implicated a large entropy term associated with formation of five-coordinate intermediate species (J. F. Endicott, J. M. Ciskowski, and C. L. Wong, work in progress; see also footnote 56).

(68) C. K. Poon, *Coord. Chem. Rev.*, **10**, 1 (1973).

(69) Y. Hung and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 4977 (1977).

(70) Based on eq 1, $k_{AB} = (k_{AA}k_{BB}K_{AB})^{1/2}$ and $k_{BA} = (k_{BB}k_{AA}K_{BA})^{1/2}$ since $\Delta G^{\circ}{}_{AB}$ is small for these reactions.

(71) There is a small ambiguity in the location of the intercept. In Figure 3 we have assumed that K'_{OS} for the Co(N$_4$)(OH$_2$)$_2^{3+,2+}$ reactions (at $\mu = 1.0$) is approximately equal to $K_{OS}k_C$ for the Co(N$_4$)(OH$_2$)Cl^{2+}/Co(N$_4$)(OH$_2$)$_2^{2+}$ reactions (at $\mu = 0.1$). A better estimate might be $5K'_{OS} \sim K_{OS}k_C$ (see Table VI) leading to a discrepancy of about 5 kJ mol^{-1} in the location of zero on the abscissa. Equilibria are as defined in Scheme I.

(72) This is plausible since there is only a small change in dipole moment within the very bulky inner-sphere precursor complex. Of course this is also expected when (as here) $(a + b) > r$ in eq 21, using

$$\lambda_o = e^2\left(\frac{1}{2a} + \frac{1}{2b} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)$$

(see ref 2c–f and 3). D_{op} and D_s are the optical and static dielectric constants of the aqueous medium (see ref 3). A probably more accurate and even smaller value of λ_o may be obtained using an ellipsoidal model of the interpenetrating spheres of the inner-sphere precursor complex: R. D. Cannon, *Chem. Phys. Lett.*, **49**, 299 (1977). Unfortunately r is not an easily estimated parameter in the inner-sphere systems we have examined.

(73) R. A. Marcus, *Discuss. Faraday Soc.*, **29**, 118 (1960).

(74) J. A. Stritar and H. Taube, *Inorg. Chem.*, **8**, 2281 (1969).

(75) A. G. Sykes, "Kinetics of Inorganic Reactions", Pergamon Press, Oxford, 1966, pp 183–188.

Reaction of a Tetraaza[14]annulene Cobalt(III) Complex with Acetylene. Synthesis and Structural Characterization of a Novel Cobalt(III) Complex Containing a Pentadentate Macrocyclic Ligand with a Carbon σ-Donor Atom: [(7-(*cis*-β-Vinylide)-7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*]-[1,4,8,11]tetraazacyclotetradecinato)pyridinecobalt(III)] Hexafluorophosphate Monoacetonitrile

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Abstract: The cycloaddition reaction of acetylene with Co(III) complexes of the 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato ligand yields a novel, dianionic pentadentate macrocycle with four equatorial nitrogen donor atoms and a vinylide carbon σ donor occupying one axial site. The Co(III) complex containing this ligand, $[Co(C_{24}H_{24}N_4)(C_5H_5N)]PF_6 \cdot CH_3CN$, crystallizes in the monoclinic space group *Pc* with cell parameters $a = 10.644$ (2) Å, $b = 8.309$ (2) Å, $c = 18.614$ (5) Å, $\beta = 107.7$ (1)°, and $Z = 2$. The structure was refined by Fourier and least-squares techniques to conventional and weighted *R* values of 4.1 and 4.7%, respectively, based on 4490 unique data with $|F_o| \geq 3\sigma|F_o|$. The acetylene has added across one six-membered 2,4-pentanediiminato chelate ring bridging the cobalt atom and the methine carbon. The resultant macrocycle contains a bicyclic, tridentate chelate with pentane-2,4-diimine-3-vinylide functionalities and an unmodified 2,4-pentanediiminato chelate ring. The Co(III) atom lies in the N_4 donor atom plane with an average Co–N distance of 1.892 Å. The Co–C(vinylide) distance is 1.908 Å. The long Co–N(pyridine) distance of 2.098 Å is attributable to a combination of a trans effect and steric interactions. The importance of peripheral steric interactions within the ligand on the details of the macrocyclic ligand conformation and the role these play in the formation of the complex are discussed. Structural comparisons are made with other Co(III)–vinyl species and with Co(III) porphyrin complexes.

Introduction

The reactions of cobalt macrocyclic systems have aroused interest because of their ability to model phenomena in biologic systems. The activation of carbon-containing compounds for isomerization and alkyl-transfer reactions is known to occur in situ in the biosphere and has been modeled in various coenzyme B_{12} analogue species.[2-4] Consequently structural studies of unsaturated macrocyclic systems have proven to be informative and to sometimes yield important results. The most notable case, was the full structural characterization of vitamin B_{12} by Lenhert and Crowfoot-Hodgkin.[5] This elucidation of a naturally occurring, stable Co–C bonded species prompted the search for related synthetic organotransition metal complexes.

Synthetic schemes attempting to model B_{12} behavior have resulted in novel structures and reactions. For example, the

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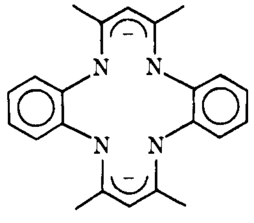
Table I. Crystal Data for $[Co(C_{24}H_{24}N_4)(C_5H_5N)]PF_6{\cdot}CH_3CN$

mol wt	692.53
space group	Pc
cell constants	
a, Å	10.644 (2)
b, Å	8.309 (2)
c, Å	18.614 (5)
α, deg	90.0
β, deg	107.7 (1)
γ, deg	90.0
No. of reflections used to determine cell constants and their 2θ limits, deg	28 $40 < 2\theta < 50$
Z	2
ρ_{calcd}, g cm^{-3}	1.466
ρ_{exptl}, g cm^{-3}	1.47
μ, cm^{-1}	6.93
absorption correction	no

reaction of the supernucleophilic species $[Co(I)(dmg)_2]$ with 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane (DDT) yielded the complex [1-chloro-2,2-bis(p-chlorophenyl)vinyl]bisdimethylglyoximato(pyridine)cobalt(III), $[Co(dmg)_2(py)(vinyl)]$.[6,7] Presumably the dehydrohalogenation follows the S_N2 attack of the Co(I) species on the DDT displacing a chloride ion. Other, more directed studies have been developed aimed at modifying the cobaloxime core, i.e., $[Co(dmg)_2]$. The synthetic modifications yielded two types of pentadentate ligand which have, in addition to the bisdimethylglyoximato N donors, a carbon (sp^3) σ-donor atom as one of the axial ligands. The resulting Co(III)-alkyl species have been structurally characterized and interesting rearrangements have been studied which mimic coenzyme B_{12} activity.[8]

The Co(II) and Co(III) complexes containing the macrocyclic ligand 7,16-dihydro-6,8,15,17-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato (I) have been



I

shown to be extremely versatile with respect to the range of skeletal modifying reactions which take place.[9] The complex, containing an appended, pentadentate macrocycle formed by the reaction of acetylene with the bispyridinato Co(III) species, $[Co(C_{22}H_{22}N_4)(C_5H_5N)_2]^+$, was examined for the following reasons: (1) the novelty of having a carbon (sp^2) σ donor fixed to a macrocyclic core, and (2) the examination of the resultant structural strain expected in the macrocyclic moiety. Also, the trans-labilizing effect of the vinyl carbanion on the axial pyridine was expected to be structurally significant and to correlate with the solution ^{1}H NMR spectra.[9]

Experimental Section

Materials. All of the chemical reagents and solvents used were obtained from commercial sources and were of reagent grade.

Preparation of $[Co(C_{24}H_{24}N_4)(C_5H_5N)]PF_6{\cdot}CH_3CN$. The free ligand was prepared as previously reported.[19] To a stirred slurry of 1.0 g (2.9 × 10^{-3} mol) of $C_{22}H_{24}N_4$, the free ligand, in 10 mL of acetonitrile, deoxygenated by saturating the mixture with acetylene, was added 0.75 g (3.0 × 10^{-3} mol) of $Co(OAc)_2{\cdot}4H_2O$ in 6 mL of degassed methanol. The four-coordinate complex $[Co(C_{22}H_{22}N_4)]$ slowly formed and precipitated from the solution while the temperature of the reaction vessel was maintained at 25 °C. A slow stream of oxygen was then passed through the stirred mixture for 1 min. Immediately the solution turned dark green and most of the precipitate redissolved. The solution was filtered to remove any unreacted solid, followed by the addition of 1 mL of pyridine to the filtrate. To this solution was added a twofold excess of NH_4PF_6 in 10 mL of water. The product crystallized from solution as dark red crystals which are green on powdering. The solid was filtered, washed with cold methanol, washed with distilled water, and dried in a stream of dry nitrogen. The complex was recrystallized by dissolution in a minimum amount of acetonitrile-pyridine (20/1 v/v) and filtering the solution, followed by the slow addition of water, yield 45-65%. See ref 9 for ^{1}H NMR spectrum.

Table II. Data Collection and Refinement Details for $[Co(C_{24}H_{24}N_4)(C_5H_5N)]PF_6{\cdot}CH_3CN$

diffractometer	Picker FACS-1
monochromater (Bragg angle, deg)	graphite, 6.093
radiation, Å	Mo K$\bar{\alpha}$, 0.710 69
take-off angle, deg	3.0
method	θ–2θ
scan speed, deg min^{-1}	2.0
scan width, deg	2.0
background time, s	2 × 10
no. of standards	3
2θ limits of data, deg	$0 < 2\theta < 60$
no. of data collected	5137
no. of data used in final refinement	4490, $\lvert F_o\rvert > 3\sigma(F_o)$
no. of data/no. of variables, NO/NV	11.7
$R_1 = [\Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert]^a$	0.041
$R_2 = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w(F_o)^2]^{1/2}$	0.047
standard error of an observation of unit weight, electrons = $[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(NO - NV)]^{1/2}$	2.116
max residual electron density on final difference Fourier map, e/Å^3	0.358

[a] Function minimized = $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ where $w = 1/\sigma(F_o)^2$.

Note: The same product can be obtained by starting with the bispyridinato Co(III) complex, $[Co(C_{22}H_{22}N_4)(C_5H_5N)_2]PF_6$. However, the procedure described is simpler because it is unnecessary to isolate any of the Co(III) intermediates.

Preparation of $[Co(C_{24}H_{24}N_4)(C_5H_5N)]Cl{\cdot}CH_3OH$. The synthesis of this compound was exactly as that described above, except that NH_4Cl in water was added instead of NH_4PF_6.

Crystal Examination of $[Co(C_{24}H_{24}N_4)(C_5H_5N)]Cl{\cdot}CH_3OH$. A crystal suitable for X-ray diffraction studies was selected. Precession photographs indicated that the crystals belonged to the monoclinic system with systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, indicating $P2_1/c$ as the unique space group. Examination of many of these crystals showed that they rapidly decomposed in a matter of hours, presumably owing to the loss of solvent methanol. Consequently, the complex with Cl^- as anion was not further utilized in structural examination.

Crystal Examination and Data Collection. $[Co(C_{24}H_{24}N_4)(C_5H_5N)]PF_6{\cdot}CH_3CN$. A crystal 0.50 × 0.40 × 0.35 mm, suitable for X-ray diffraction studies, was selected. Precession photographs indicated the monoclinic system with systematic absences $h0l$, $l = 2n + 1$, suggesting either $C_s{}^2$-Pc or $C_{2h}{}^4$-$P2/c$ as the correct space group.[10] Refined cell constants and other pertinent crystal data are presented in Table I.[11]

Intensity data were collected on a Picker FACS-1 automated diffractometer. A symmetrical dispersion factor of 0.692 was used at increasing values of 2θ to account for α_1-α_2 splitting. During the course of data collection, three standard reflections were measured every 100 data to monitor crystal quality and alignment. The routine aspects of data collection are presented in Table II.

Relative intensities and their deviations are calculated by $I = S - tB$ and $\sigma(I) = [S + t^2B + p^2(S + tB)^2]^{1/2}$ where S is the total peak scan counts, B is the total background counts, t is the ratio of peak to background scan times, and p is an "instability" constant, here taken as 0.01, to account for machine fluctuation and other sources of error which would be expected to result in variations proportional to the diffracted intensity.[12,13] The observed structure factor amplitudes and their standard deviations were calculated by $F_o = (I/Lp)^{1/2}$ and $\sigma(F_o)$

Table III. Nonhydrogen Atom Positional Parameters for $[Co(C_{24}H_{24}N_4)(C_5H_5N)]PF_6 \cdot CH_3CN$

atom	x	y	z
Co	0.0	0.7333 (5)	0.0
P	0.4846 (1)	0.3949 (2)	−0.1278 (1)
F1	0.3845 (6)	0.3085 (8)	−0.1953 ()
F2	0.4052 (5)	0.3398 (9)	−0.0741 (4)
F3	0.5883 (6)	0.4789 (8)	−0.0642 (3)
F4	0.5681 (5)	0.4388 (9)	−0.1794 (3)
F5	0.5650 (5)	0.2405 (6)	−0.1049 (3)
F6	0.4030 (6)	0.5485 (6)	−0.1491 (5)
N1	−0.1306 (3)	0.0165 (4)	−0.0913 (2)
N2	−0.1221 (3)	0.1393 (4)	0.0495 (2)
N3	0.1277 (3)	0.1306 (5)	0.0913 (2)
N4	0.1197 (3)	0.0114 (4)	−0.0520 (2)
N5	0.0041 (3)	0.3074 (4)	−0.0414 (2)
C1	−0.2400 (3)	−0.0463 (4)	−0.0909 (2)
C2	−0.2521 (4)	−0.0780 (5)	−0.0129 (2)
C3	−0.2329 (3)	0.0678 (5)	0.0378 (2)
C4	−0.0636 (4)	0.2556 (5)	0.1060 (2)
C5	−0.1278 (4)	0.3753 (5)	0.1318 (2)
C6	−0.0546 (6)	0.4827 (6)	0.1867 (3)
C7	0.0793 (6)	0.4688 (6)	0.2128 (3)
C8	0.1454 (4)	0.3530 (6)	0.1856 (2)
C9	0.0757 (4)	0.2438 (5)	0.1309 (2)
C10	0.2483 (4)	0.0663 (5)	0.1122 (2)
C11	0.2965 (3)	−0.0192 (6)	0.0611 (2)
C12	0.2426 (4)	−0.0343 (5)	−0.0167 (2)
C13	0.0606 (4)	0.0300 (4)	−0.1303 (2)
C14	0.1242 (4)	0.0638 (5)	−0.1840 (2)
C15	0.0507 (6)	0.0969 (6)	−0.2571 (2)
C16	−0.0862 (5)	0.1003 (5)	−0.2788 (2)
C17	−0.1503 (4)	0.0735 (5)	−0.2261 (2)
C18	−0.0790 (4)	0.0365 (4)	−0.1525 (2)
C19	−0.3465 (4)	−0.1107 (6)	−0.1569 (2)
C20	−0.3354 (4)	0.1040 (6)	0.0755 (2)
C21	0.3394 (4)	0.0755 (7)	0.1926 (2)
C22	0.3305 (4)	−0.1080 (6)	−0.0585 (3)
C23	−0.0174 (4)	−0.1394 (5)	0.0345 (2)
C24	−0.1384 (4)	−0.1944 (4)	0.0248 (2)
C25	−0.1050 (4)	0.3858 (5)	−0.0780 (2)
C26	−0.1036 (6)	0.5275 (6)	−0.1141 (3)
C27	0.0108 (6)	0.5928 (7)	−0.1135 (3)
C28	0.1224 (5)	0.5171 (6)	−0.0765 (3)
C29	0.1174 (4)	0.3767 (5)	−0.0411 (3)
N6	−0.3864 (7)	0.2954 (9)	−0.3763 (4)
C30	−0.4626 (7)	0.3834 (9)	−0.3771 (5)
C31	−0.5683 (12)	0.4834 (15)	−0.3743 (7)

$= [(I + \sigma(I))/Lp]^{1/2} - (I/Lp)^{1/2}$ where Lp is the Lorentz and polarization correction under the condition of monochromated radiation.[14] An absorption correction was not applied and an analysis of the standards indicated that small changes in integrated intensities (<3%) occurred during data acquisition.

Solution and Refinement of the Structure. Normalized structure factor amplitudes were calculated by Wilson's method and an analysis of the E data indicated a noncentrosymmetric structure.[15] Therefore, initially, space group Pc was used during the solution of the structure. Both the phosphorus and cobalt atoms were located on a Patterson map. A structure factor calculation with these two atoms gave conventional and weighted R values of 0.382 and 0.492, respectively.[16] Next a Fourier map was calculated based on observed structure factor amplitudes and the phases from the two heavy atoms. Two sets of macrocyclic nitrogen atoms resulting from the persistent pseudoinversion center located at the cobalt atom were located on the map. The correct image was chosen after Fourier and least-squares refinement of each set—the correct image revealed the rest of the macrocyclic moiety, while the incorrect image revealed one with unreasonable bond distances and angles. All nonhydrogen atoms, including the solvate acetonitrile and PF_6^- anion, were located by Fourier, difference Fourier, and least-squares techniques. After two cycles of full-matrix least-squares refinement varying positional and anisotropic thermal parameters for the cobalt and phosphorus atoms and positional and isotropic thermal parameters for all other nonhydrogen atoms, the conventional and weighted R values were reduced to 0.078 and 0.079, respectively. A difference Fourier map revealed the positions of all the hydrogen atoms in the asymmetric unit. Final hydrogen atom positions were calculated assuming standard geometries with C–H bond distances of 0.95 Å,[17] with least-squares refinement of the methyl hydrogen atom positions, macrocyclic and solvate, fitting the trial coordinates to standard tetrahedral geometry. All hydrogen atoms were assigned isotropic thermal parameters of $B = 3.5$ Å^2 and were included as fixed contributions in the final least-squares refinement.

Because of the large number of variables, the structure was divided into three equal sized groups of contiguous atoms, not including the cobalt and phosphorus atoms. Three cycles of blocked-matrix least-squares refinement were then calculated with the positional and anisotropic thermal parameters varied for two of the three groups of each cycle. The cobalt and phosphorus parameters were varied every cycle. In this way every parameter was varied at least twice and all pairs of parameters were varied simultaneously at least once. There were no correlation coefficient greater than 0.5. Convergence was indicated by the near insignificant changes in each parameter the second time it was varied. At convergence the conventional and weighted R values were 0.041 and 0.047, respectively, for 4490 data with $|F_o| > 3\sigma(F_o)$. Refinement details and final discrepancy indices are given in Table II. A maximum residual electron density of 0.36 e/Å^3 was located on the final difference Fourier map near the PF_6^- anion. The final positional parameters, along with their estimated standard deviations, are listed in Table III. The neglect of correlations in the blocked re-

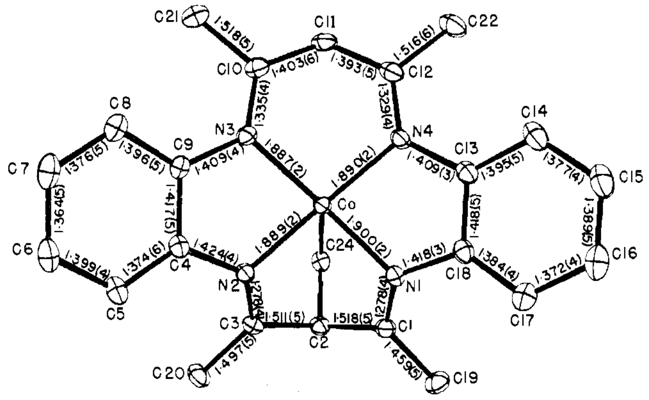


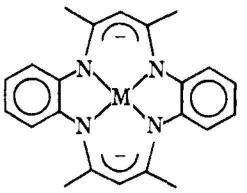
Figure 1. Projection down the Co-C23 bond axis of $[Co(C_{24}H_{24}N_4)(C_6H_5N)]^+$ illustrating the labeling scheme and the interatomic distances within the ligand and the equatorial coordination sphere. The pyridine ligand has been omitted for clarity of presentation. The thermal ellipsoids are drawn at the 20% probability level.

finement may result in a small underestimation of the least-squares deviations from those indicated. A listing of the thermal parameters, hydrogen atom coordinates, and observed and calculated structure factor amplitudes is given as supplementary material (see paragraph at end of paper).

Results and Discussion of the Structure

General Comments. The asymmetric unit contains the complex cation, a PF_6^- anion, and an acetonitrile solvate molecule. As predicted, the complex cation contains a dianionic, pentadentate, macrocyclic moiety surrounding the central Co(III) atom with the sixth coordination site occupied by a pyridine molecule. The PF_6^- anion and the acetonitrile solvate are distributed in lattice cavities formed by the packing of the large complex cations. The bond distances and angles in the PF_6^- anion and the acetonitrile solvate are within normal ranges (Table V). Average values for the anion are P-F = 1.538 Å, F-P-F = 90.0°. The closest contacts of the PF_6^- anion with the complex cation are the nonbonded distances between F5 and the atoms C1, C3, and C19 (3.118 (6), 3.206 (6), and 3.200 (7) Å, respectively) and are associated with the tridentate, pentane-2,4-diimine-3-vinylide chelate ring. The acetonitrile solvate has no significant interaction with the complex cation or the PF_6^- anion.

Basically, the complex cation is a saddle-shaped macrocyclic moiety similar to that observed in numerous transition metal complexes of the precursor macrocycle 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato.[18,20,23]



A view of the complex cation normal to the plane containing the equatorial nitrogen donor atoms is shown in Figure 1 along with an atomic labeling scheme and selected intraatomic distances within the macrocycle and equatorial coordination sphere. A side view of the complex cation is shown in Figure 2 illustrating the warping of the ligand and the axial contents of the coordination sphere, along with the pertinent atom labels, bond distances, and angles. The packing arrangement of the complex cation, PF_6^- anion, and the acetonitrile solvate is shown in the stereodiagram in Figure 3. Selected bond angles are listed in Table IV. Bond distances in the PF_6^- anion, the acetonitrile solvate, and the pyridine molecule are listed in Table V.

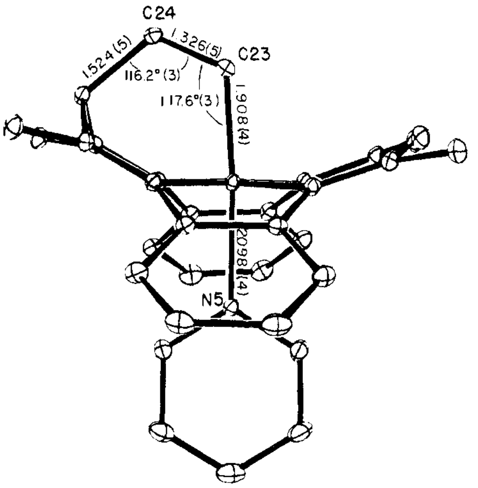
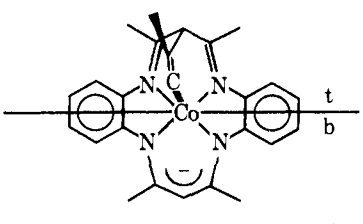


Figure 2. Side view of $[Co(C_{24}H_{24}N_4)(C_5H_5N)]^+$ illustrating the saddle shape of the ligand and the vinylide bridge. Thermal ellipsoids are drawn at the 20% probability level.

The Macrocyclic Ligand. The complex cation contains a novel, dianionic, pentadentate macrocycle with four equatorial nitrogen donor atoms and a vinylide carbon σ-donor atom occupying one axial site. Formally the parent macrocyclic species, $[Co(C_{22}H_{22}N_4)(py)]^+$, has undergone a cycloaddition reaction with acetylene such that the acetylene molecule has added across one six-membered, 2,4-pentanediiminato chelate ring bridging the cobalt atom and the methine carbon. The resultant macrocycle contains a bicyclic, tridentate chelate with pentane-2,4-diimine-3-vinylide functionalities and an unmodified 2,4-pentanediiminato (≡ bidentate) chelate ring (vide infra). These tridentate and bidentate chelate rings are separated from the aromatic benzenoid rings by the nominally single C-N bonds in the five-membered chelate rings. The benzenoid rings are rigorously planar; the largest deviations from the planes are 0.019 and 0.014 Å for C4-C5-C6-C7-C8-C9 and C13-C14-C15-C16-C17-C18, respectively.

While the complex cation has no rigid crystallographic symmetry, it can be seen on inspection of bond distances and angles that approximate mirror symmetry relates chemically equivalent halves of the cation; the mirror plane contains the pyridine molecule, the Co atom, the vinylide residue (C23=C24), and atoms C2 and C11. It will be useful to consider the two nonequivalent bidentate and tridentate chelating moieties and their associated bond parameters in an analysis of the pentadentate macrocycle. Where confusion involving parameters may occur, those labeled with a subscript t refer to the tridentate chelate and those labeled with a subscript b refer to the bidentate chelate. The subscript also serves to delineate the nonequivalent halves of the macrocycle divided by a plane, containing the Co atom, bisecting the macrocycle as shown below.



The side view of the molecule shown in Figure 2 reveals a marked deformation of the macrocyclic skeleton. Most of the configurational adaptation has occurred to accommodate the Co atom lying in the plane formed by the equatorial nitrogen atoms. There are three major factors governing the ligand conformation: (1) the steric interactions of the methyl groups

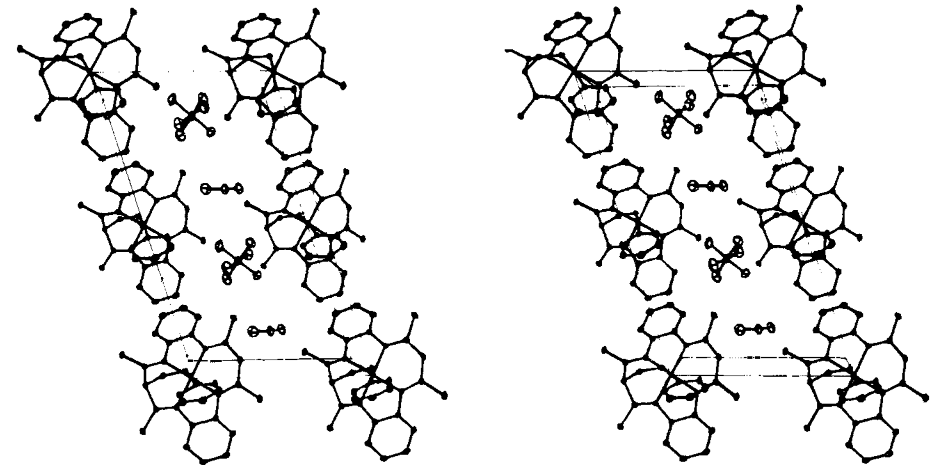


Figure 3. Stereodiagram of the packing arrangement of $[Co(C_{24}H_{24}N_4)(C_5H_5N)]PF_6{\cdot}CH_3CN$ as viewed down the crystallographic *b* axis. The thermal ellipsoids are drawn at the 10% probability level.

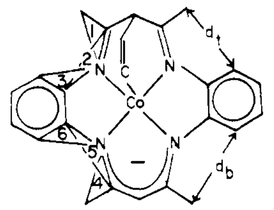


Figure 4. Diagrammatic key to aid in the interpretation of parameters summarized in Table VII.

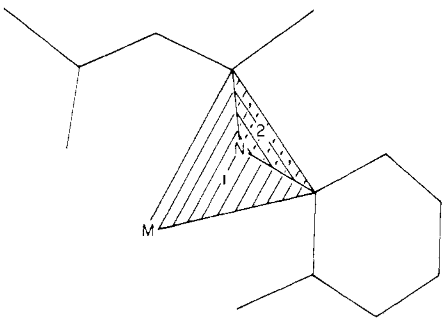


Figure 5. Diagram illustrating the planes used to evaluate the dihedral angles and the extent of mismatch between the metal and ligand σ orbitals.

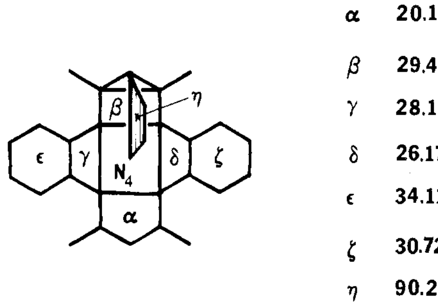


Figure 6. Illustration of various planes formed by the chelate and benzenoid rings, along with the dihedral angle between each plane and the N_4 donor plane.

with the benzenoid rings; (2) the directionality of the equatorial nitrogen atom lone pair electrons into favorable overlap with the appropriate Co orbitals; and (3) the maintenance of planarity in the quasi-aromatic 2,4-pentanediiminato (bidentate) chelate ring. These interrelated aspects will be examined in detail.

The relief of peripheral steric strain is achieved mainly through torsional twists about the C-N bonds in the various chelate rings—tridentate, bidentate, and the five-membered rings. The dihedral angles defining the torsional twists are listed in Table VI and the average values are summarized in Table VII and Figure 4. The tridentate, or t, half of the macrocycle will be considered first.

The steric interactions of the methyl groups with the benzenoid rings are relieved primarily through large torsional twists of 32.5° about the $C{-}N_t$ bonds in the five-membered chelate rings with smaller torsional twists of 5.2° about the $C{=}N_t$ imine bonds. The peripheral steric crowding as well as the rigidity of the tridentate chelate contributes to these torsional twists. As a result of the torsional deformation, the average methyl-benzenoid contact d_t (Table VII) of 3.134 Å is in the range normally equated with repulsive interactions. However, the sp^2-hybridized N atom lone pairs are slightly misdirected by an average value of 6.2°. This extent of Co-N σ bond mismatch is estimated by considering the dihedral angle between planes defined by C-M-C and C-N-C in Figure 5.

The torsional twists in the bidentate (2,4-pentanediiminato), or b, half are exactly what one would predict from the trends established in the structural study of the series of five-coordinate complexes with the parent macrocycle.[18] The metal lies within the N_4 plane within one estimated standard deviation (±0.011 Å). Consequently the twists about the $C{-}N_b$ bonds in the five-membered chelate rings are a small 24.7°, compromising the steric relief but directing the N(macrocycle) lone pairs into the macrocyclic N_4 plane. Prevention of severe peripheral steric strain is, therefore, dependent upon large torsional twists about the $C{-}N_b$ bonds in the bidentate chelate (2,4-pentanediiminato ring) of 14.5°. These values are comparable to those observed in the four- and six-coordinate Fe(II) complexes containing the parent macrocycle $[Fe(C_{22}H_{22}N_4)]$[23] and $[Fe(C_{22}H_{22}N_4)(CO)py]$.[19,20] As a result of these twists, the minimum methyl-benzenoid contact, d_b, is 3.053 Å and the concomitant Co-N σ bond mismatch is 1.4°. However, the π delocalization in the chelate ring is probably compromised because the Co atom is displaced by 0.443 Å from the plane formed by the 2,4-pentanediiminato chelate atoms N3-C10-C11-C12-N4.

The overall conformation of the pentadentate macrocycle can be described by considering the dihedral angles between the various chelate and benzenoid rings and the macrocyclic N_4 plane (Figure 5). The distribution of angles is such that the Co atom is accommodated in the N_4 plane and the N5-Co-C23 bond axis is approximately linear placing the $C(sp^2)$ σ

Table IV. Interatomic Angles (deg) for [Co($C_{24}H_{24}N_4$)(C_5H_5N)]PF_6·CH_3CN

N1-Co-N2	94.76 (2)	N4-C12-C11	121.4 (3)
N2-Co-N3	84.37 (2)	N4-C12-C22	122.0 (3)
N3-Co-N4	96.68 (2)	C11-C12-C22	116.6 (4)
N1-Co-N4	84.19 (2)	N4-C13-C14	127.0 (3)
N1-Co-C23	87.2 (1)	N4-C13-C18	114.0 (3)
N2-Co-C23	87.3 (1)	C14-C13-C18	118.4 (3)
N3-Co-C23	92.7 (1)	C13-C14-C15	119.7 (3)
N4-Co-C23	94.0 (1)	C14-C15-C16	121.5 (2)
N1-Co-N5	89.60 (1)	C15-C16-C17	119.7 (2)
N2-Co-N5	90.25 (2)	C16-C17-C18	120.1 (3)
N3-Co-N5	90.42 (2)	N1-C18-C13	112.8 (3)
N4-Co-N5	88.39 (1)	N1-C18-C17	126.3 (3)
N5-Co-C23	175.8 (1)	C13-C18-C17	120.6 (3)
Co-N1-C1	121.2 (2)	Co-C23-C24	117.6 (3)
Co-N1-C18	109.5 (1)	C23-C24-C2	116.2 (3)
C1-N1-C18	128.9 (2)	Co-N5-C25	121.8 (2)
Co-N2-C3	121.1 (2)	Co-N5-C29	121.2 (2)
Co-N2-C4	110.2 (1)	C25-N5-C29	116.4 (3)
C3-N2-C4	128.0 (2)	N5-C25-C26	122.0 (3)
Co-N3-C9	110.5 (1)	C25-C26-C27	120.2 (3)
Co-N3-C10	121.9 (2)	C26-C27-C28	118.8 (3)
C9-N3-C10	127.6 (2)	C27-C28-C29	119.9 (3)
Co-N4-C12	122.7 (2)	C28-C29-N5	122.8 (3)
Co-N4-C13	109.9 (1)	N6-C30-C31	173.3 (12)
C12-N4-C13	127.3 (2)	F1-P-F2	90.6 (3)
N1-C1-C2	117.4 (3)	F1-P-F4	89.4 (3)
N1-C1-C19	127.3 (3)	F1-P-F5	91.5 (4)
C2-C1-C19	117.4 (3)	F1-P-F6	88.8 (4)
C1-C2-C3	115.0 (3)	F2-P-F3	92.4 (4)
C1-C2-C24	105.1 (3)	F2-P-F5	86.7 (3)
C3-C2-C24	106.3 (3)	F2-P-F6	92.0 (4)
N2-C3-C2	115.0 (3)	F3-P-F4	87.5 (3)
N2-C3-C20	126.3 (3)	F3-P-F5	87.4 (3)
C2-C3-C20	118.3 (3)	F3-P-F6	92.3 (4)
N2-C4-C5	126.7 (3)	F4-P-F5	89.6 (4)
N2-C4-C9	112.1 (3)	F4-P-F6	91.7 (4)
C5-C4-C9	121.1 (4)		
C4-C5-C6	119.3 (4)		
C5-C6-C7	119.9 (2)		
C6-C7-C8	121.5 (2)		
C7-C8-C9	120.3 (4)		
N3-C9-C4	114.4 (4)		
N3-C9-C8	127.6 (3)		
C4-C9-C8	117.8 (4)		
N3-C10-C11	121.5 (3)		
N3-C10-C21	122.5 (4)		
C11-C10-C21	116.0 (4)		
C10-C11-C12	129.1 (3)		

Table V. Bond Distances (Å) for Coordinated Pyridine, Solvent Acetonitrile, and Anion PF_6 in [Co($C_{24}H_{24}N_4$)(C_5H_5N)]PF_6·CH_3CN

A. Pyridine	
N5-C25	1.333 (4)
C25-C26	1.360 (4)
C26-C27	1.330 (5)
C27-C28	1.336 (5)
C28-C29	1.349 (5)
C29-N5	1.334 (4)
B. Acetonitrile	
N6-C30	1.089 (8)
C30-C31	1.412 (12)
C. PF_6[a]	
P-F1	1.554 (5)
P-F2	1.560 (5)
P-F3	1.522 (5)
P-F4	1.538 (5)
P-F5	1.529 (4)
P-F6	1.527 (5)

[a] The P-F distances are probably less reliable than indicated by the esd's because of high thermal and/or librational motions.

donor in the axial coordination site. Note that the plane containing the vinylide residue (C23=C24), C2, and the Co atom is almost perpendicular (90.28°) to the macrocyclic N_4 plane. The pyridine ligand is inclined 8.88° from the plane perpendicular to the macrocyclic N_4 plane.

Bonding parameters in the macrocycle are within normal ranges (see Table VII for a summary of important, averaged bond distances). Carbon-carbon bond lengths, 1.497-1.524 Å, are within normal range, but there is one short bond length of 1.459 Å for C1-C19. The average imine bond length, 1.278 Å, is comparable to those observed in the related [Co(N_4)-(vinyl)py] complexes where (N_4) is dimethylglyoxime,[6,7] salen *N,N'*-ethylenebissalicylidineiminato),[21] or BAE (*N,N'*-thylenebisacetylacetoneiminato).[22] The C-N bond distances n the five-membered chelate rings are 1.421 Å for C-N_b and 1.409 Å for C-N_t, well within the range of values in related complexes, and imply a high degree of single-bond character. The bond parameters in the unmodified bidentate (2,4-pentanediiminato) chelate ring are similar to those in the closely related isoelectronic Fe(II) species [Fe($C_{22}H_{22}N_4$)][23] and [Fe($C_{22}H_{22}N_4$)(CO)py].[20] The vinylide double bond, 1.326 Å, is comparable to that in related Co-vinyl complexes (Table

Table VI. Selected Dihedral Angles (deg) for $[Co(C_{24}H_{24}N_4)(C_5H_5N)]PF_6{\cdot}CH_3CN$

A. Defining Planes between N1-N2-N3-N4 and	
N3-C10-C11-C12-N4	20.18
N1-C1-C3-N2	29.45
N1-C18-C13-N2	28.11
N2-C4-C9-N3	26.17
C4-C5-C6-C7-C8-C9	30.72
C13-C14-C15-C16-C17-C18	34.11
Co-C23-C24-C2	90.28
B. Atoms Defining Planes	
C22-C12-N4 C12-N4-C13	13.4 (5)
C12-N4-C13 N4-C13-C14	25.9 (5)
C21-C10-N3 C10-N3-C9	15.6 (5)
C10-N3-C9 N3-C9-C8	23.5 (5)
C19-C1-N1 C1-N1-C18	2.6 (5)
C1-N1-C18 N1-C18-C17	36.7 (5)
C20-C3-N2 C3-N2-C4	7.7 (5)
C3-N2-C4 N2-C4-C5	37.5 (5)

Table VII. Summary of Important Parameters for $[Co(C_{22}H_{22}N_4)(C_5H_5N)]PF_6{\cdot}CH_3CN$

av Co-N (≡ Ct-N) distance, Å	1.892
Co-N axial distance, Å	2.098
Co-C axial distance, Å	1.908
av distances, Å, in tridentate chelate	
$C{=}N_t$	1.278
$C{-}C_t$	1.517
$C{=}C_t$	1.326
av distances, Å, in bidentate chelate	
$C{-}N_b$	1.332
$C{-}C_b$	1.398
av distances, Å, in five-membered rings	
$C{-}N_t$	1.409
$C{-}N_b$	1.412
av dihedral angle, deg[a]	
1-2	5.2
2-3	32.5
4-5	14.5
5-6	24.7
av nonbonded distance, Å[a]	
d_t	3.134
d_b	3.053

[a] Refer to Figure 4 for the key.

VIII summarizes the Co-C, Co-N(axial), and C=C bond lengths for the Co-vinyl complexes and Co-C and Co-N(axial) bond lengths for two related complexes containing pentadentate ligands with saturated C(sp^3) σ donors). The Co-C23-C24 angle is 117.6°, considerably less than the average 128.45° observed for the unrestrained Co-vinyl complexes.

Inner Coordination Sphere and Axial Ligand Geometry. Since the Co(III) atom fits into the macrocyclic core with no deviation from the N_4 plane, the average Co-N(macrocycle) distance of 1.892 Å is fixed by the rigidity of the macrocyclic skeleton. The N-Ct distance observed in the pentadentate ligand is similar to that observed in complexes of the parent ligand,[20,23] and allows Co-N(macrocycle) distances in the range commonly observed for Co(III) complexes containing unsaturated amine ligands such as dimethylglyoximato, salen, and BAE.[24,25] The average distance in the isoelectric complex $[Fe(C_{22}H_{22}N_4)(CO)py]$[20] is 1.942 Å.

As can be seen in Table VIII the Co-C bond distance is shorter than in related vinyl complexes with transpyridine ligands. This is probably a consequence of the limitation imposed by the rigidity in the macrocyclic tridentate chelate. The N5-Co-C23 angle, 175.8°, departs slightly from linearity demonstrating the limited flexibility of the appended vinylide residue. The short Co-C bond length has the effect of placing H23 (the vinylic hydrogen atom attached to the σ-donating 23) only 2.56 Å above the bidentate chelate ring (N3-C10-C11-C12-N4).

The Co-N(pyridine) axial bond distance, 2.098 Å, is long compared to the 1.88-1.97 Å observed in Co(III) amine complexes, the elongation resulting from combined electronic and steric factors.[25] The trans-labilizing influence is well characterized, both structurally and kinetically,[26] for ligands trans to carbon σ-donating atoms. For example, the Co-N(pyridine) bond distance in [Co(salen)(OMe)py] is 2.031 Å,[27] while the Co-N bond is elongated to 2.119 Å in the related alkyl complex [Co(salen)py(vinyl)].[21,28]

Another effect influencing the Co-N(pyridine) bond length is the steric crowding caused by the interaction of the pyridine α-hydrogen atoms with the macrocyclic nitrogen donor atoms and the carbon skeleton. Primarily the steric stress is relieved by orienting the pyridine ligand so that the pyridine plane is approximately parallel to the plane containing C2-Co-C11. The pyridine is thus efficiently tucked into a pocket formed by the ligand conformation. The average pyridine αC-N(macrocycle) contact is 3.12 Å, while the average αH-N(macrocycle) contact is 2.80 Å. These H-N contacts are slightly smaller than the sum of the H and N van der Waals radii (2.90 Å); therefore, the axial Co-N(pyridine) lengthening may have a steric component. Indeed, the related Fe(II) complex $[Fe(C_{22}H_{22}N_4)(CO)py]$[20] contains a remarkably elongated Fe-N(pyridine) bond length of 2.088 Å, the usual trans effect

Table VIII. Structural Parameters for $[Co(C_{24}H_{24}N_4)(C_5H_5N)]PF_6{\cdot}CH_3CN$ and Some Related Compounds

compd	Co-C, Å[a]	$Co{-}N_a$, Å[b]	C=C, Å[c]	Co—C=C-, deg	ref
$[Co(C_{24}H_{24}N_4)(C_5H_5N)]PF_6{\cdot}CH_3CN$	1.908 (4)	2.098 (4)	1.326 (5)	117.6 (3)	this work
A. σ-Vinyl Donor Compounds					
[Co(salen)py(vinyl)][d]	1.93 (2)	2.12 (1)	1.31 (3)	124.6 (13)	21
[Co(BAE)aquo(vinyl)][e]	1.89 (1)		1.33 (2)	127.2 (9)	22
[Co(dmg)py(vinyl)][f]	1.970 (13)	2.042 (10)	1.366 (15)	133.6 (10)	30, 31
B. Five-Coordinate Macrocycles with σ-Carbon Axial Donors					
"[Co(dmg)-C]"[g]	2.05	2.09			8a
"[Co(dmg)-C′]"[g]	2.04	2.09			8b

[a] Cobalt to carbon axial bond distance. [b] Cobalt to axial nitrogen bond distance. [c] Carbon-carbon double bond distance of coordinated vinyl group, when appropriate. [d] [*N,N′*-Ethylenebis(salicylideneiminato)]pyridine(vinyl)cobalt(III). [e] [*N,N″*-Ethylenebis(acetylacetoneiminato)aquo(vinyl)cobalt(III). [f] [1-Chloro-2,2-bis(*p*-chlorophenyl)vinyl]bis(dimethylglyoximato)pyridinecobalt(III). [g] Compounds "[Co(dmg)-C]" and "[Co(dmg)-C′]" are derivatives of bis(dimethylglyoximato)cobalt(III). The synthetic modification is such that an sp^3 σ-carbon donor atom is affixed to the $(dmg)_2$ macrocyclic base through an elaborate framework and serves as an axial ligand.

(due to CO) presumably vitiated by the interaction of the pyridine α hydrogens with the macrocyclic N atoms. The same argument has been used by Lauher and Ibers to explain the elongated Co–N(axial) bonds in the complex cation $[\mathrm{Co(TPP)(Im)_2}]^+$[29] However, since complexes of the type $[\mathrm{M(C_{22}H_{22}N_4)(py)_2}]^{n+}$ have not been structurally examined, the limiting Co(III)- or Fe(III)–N(pyridine) distances and related αH–N(macrocycle) contacts can be considered in a qualitative fashion only.

Comparisons with Co(III) Porphyrin Structures. No comparable Co(III)-vinyl porphyrins have been structurally examined, so comparisons of Co–C and Co–N(axial) bond distances are precluded. It is noteworthy, however, that the larger porphyrin core can accommodate longer Co–N(macrocycle) bond distances when the metal is fixed in the donor plane. Typical values for the equatorial Co–N distances are 1.982 Å in $[\mathrm{Co(TPP)(Im)_2}]^+$,[29] and 1.978 Å for $[\mathrm{Co(TPP)(pip)}]^+$,[30] 0.090 and 0.086 Å longer than those observed in the title complex, respectively.

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Supplementary Material Available: Tables containing the anisotropic thermal parameters, the calculated hydrogen atom positions, and a listing of the observed and calculated structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

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