353.5 Hz, indicates that the trans influence of the phosphonate group increases significantly when it is fully deprotonated. The smaller reduction in ^1J(Pt–N) trans to nitrogen, from 303.7 to 293.0 Hz, indicates that the trans influence of ligand nitrogen also increases slightly when its substituents are deprotonated. J(Pt–N) trans to carboxylate O remains constant at 345 Hz when $Pt(NH_3)_2$(impaH_2-*N,O*)$^+$ (XVI) is deprotonated to $Pt(NH_3)_2$(impa-*N,O*)$^-$ (XVIII), but J(Pt–N) trans to N decreases slightly (from 303.2 to 296.0 Hz) as expected. Comparison with the coupling constants for the phosphonate-bound isomer of $Pt(NH_3)_2$(impa-*N,O*)$^-$ (XIX), 349.6 Hz trans to O and 296.9 Hz trans to N, suggests that the trans influence of carboxylate is slightly greater than that of fully deprotonated phosphonate. Therefore, the trans influence order for these three O-donor groups is $-OPO_2H^-$, $<-OPO_2 \leq -O-CO-$, which presumably is also the order of increasing Pt–O bond strength.

From the reactions summarized in Schemes II and IV, there is, in acid solution, clearly a thermodynamic preference for the chelate complex with impa carboxylate bound. This may be ascribed to the higher Pt–O bond strength in the carboxylate complex XVI relative to the protonated phosphonate complex XV. In alkaline solution, there is a preference for the phosphonate-bound isomer XIX over the carboxylate-bound isomer XVIII. This does not correspond with the trans influence order. In the absence of a large trans influence difference between the two O-donor groups, the direction of the equilibrium will be determined by more subtle factors (e.g. the solvation of the $-PO_3^{2-}$ group compared with $-CO_2^-$).

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Registry No. I, 20115-64-4; II, 100019-82-7; III, 100019-83-8; IV, 100019-84-9; VII, 100019-85-0; VIII, 100019-86-1; IX, 100019-87-2; X, 100019-88-3; XI, 100019-89-4; XIII, 100019-90-7; XV, 100019-91-8; XVI, 100019-92-9; XVII, 100019-93-0; XVIII, 100019-94-1; XIX, 100019-95-2; XX, 100019-96-3; XXI, 100019-97-4; XXII, 100019-98-5; XXIII, 100019-99-6; XXIV, 100044-33-5; XXV, 100044-42-6; XXVI, 100044-43-7; idmph$_4$, 17261-34-6; midmpH$_4$, 5995-25-5; ntmpH$_6$, 6419-19-8; impaH$_3$, 1071-83-6; $PtCl_4^{2-}$, 13965-91-8; ^{195}Pt, 14191-88-9; ^{15}N, 14390-96-6.

Contribution from the Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India, and Division of Biological Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

Ternary Metal Complexes of Anionic and Neutral Pyridoxine (Vitamin B_6) with 2,2′-Bipyridine. Syntheses and X-ray Structures of (Pyridoxinato)bis(2,2′-bipyridyl)cobalt(III) Perchlorate and Chloro(2,2′-bipyridyl)(pyridoxine)copper(II) Perchlorate Hydrate

S. P. Sudhakara Rao,[†] K. I. Varughese,[‡] and H. Manohar*[†]

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Ternary metal complexes involving vitamin B_6 with formulas $[Co^{III}(bpy)_2(PN\text{-}H)](ClO_4)_2$ and $[Cu^{II}(bpy)(PN)Cl]ClO_4\cdot H_2O$ (bpy = 2,2′-bipyridine, PN = neutral pyridoxine, PN-H = anionic pyridoxine) have been prepared for the first time and characterized by means of magnetic and spectroscopic measurements. The crystal structures of the compounds have also been determined. $[Co(bpy)_2(PN\text{-}H)](ClO_4)_2$ crystallizes in the space group $P2_1/c$ with a = 18.900 (3) Å, b = 8.764 (1) Å, c = 20.041 (2) Å, β = 116.05 (1)°, and Z = 4 and $[Cu(bpy)(PN)Cl]ClO_4\cdot H_2O$ in the space group $P\bar{1}$ with a = 12.136 (5) Å, b = 13.283 (4) Å, c = 7.195 (2) Å, α = 96.91 (2)°, β = 91.25 (3)°, γ = 71.63 (3)°, and Z = 2. The structures were solved by the heavy-atom method and refined by least-squares techniques to R values of 0.080 and 0.042 for 3401 and 2094 independent reflections, respectively. Both structures consist of monomeric units. The geometry around Co(III) is octahedral and around Cu(II) is distorted square pyramidal. In $[Co(bpy)_2(PN\text{-}H)](ClO_4)_2$, two oxygens from phenolic and 4-(hydroxymethyl) groups of PN-H and two nitrogens from each of two bpy's form the coordination sphere. In $[Cu(bpy)(PN)Cl]ClO_4\cdot H_2O$ one PN and one bpy, with the same donor sites, act as bidentate chelates in the basal plane, with a chloride ion occupying the apical position. In both structures PN and PN-H exist in the tautomeric form wherein pyridine N is protonated and phenolic O is deprotonated. However, a novel feature of the cobalt compound is that PN-H is anionic due to the deprotonation of the 4-(hydroxymethyl) group. The packing in both structures is governed by hydrogen bonds, and in the copper compound partial stacking of bpy's at a distance of ~3.55 Å also adds to the stability of the system. Infrared, NMR, and ligand field spectroscopic results and magnetic measurements are interpreted in light of the structures.

Introduction

Metal complexes of the B_6 vitamins and of the Schiff bases derived from them have been an interesting area of study in recent years.[1,2] Particularly, since the discovery of the enhanced catalytic role of metal ions in nonenzymatic reactions[3] (e.g. transamination of pyridoxamine with α-ketoglutarate) attention has been focused on complexes of Schiff bases derived from amino acids and pyridoxal (PL) [or pyridoxal phosphate (PLP)] with the aim of elucidating the mechanism of action of vitamin B_6 containing enzymes.[4-7] Considerable research has also been concerned with the ligating sites in these compounds. Many of the solution studies[7-15] and a few X-ray structural investigations[15-17] reveal that in vitamin B_6 complexes chelation occurs through phenolic oxygen and the 4-(aminomethyl) or 4-(hydroxymethyl) groups of pyridoxamine (PM) or pyridoxine (PN).[18] In Schiff base complexes also, chelation has been observed[6,19-30] through phenolic

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[†] Indian Institute of Science.

[‡] National Research Council of Canada.

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oxygen, imine nitrogen, and carboxylate oxygen. Interestingly, binding at a few other sites like pyridine nitrogen[20] or the side chain at the 5-position (hydroxymethyl oxygen[16,20] or phosphate oxygen[6,21]) is also noticed. The field derives further interest due to the possible existence of B_6 vitamins in various tautomeric forms. Protonation or deprotonation at different sites like ring nitrogen, phenolic oxygen, and 4-(aminomethyl) nitrogen may occur depending upon factors such as pH of crystallization, charge neutralization requirement, etc. A fine example is that reported by Franklin and Richardson, where copper complexes of both neutral and anionic forms of PM have been studied.[16]

Studies on ternary systems involving B_6 vitamins, on the other hand, are very few. While solution studies on such systems are meager,[31-33] to our knowledge crystallographic work is nonexistent. Hence we have taken up a systematic study of ternary transition metal complexes involving vitamin B_6. In view of the suggestion that heteroaromatic N bases like imidazole or 2,2'-bipyridyl (bpy) enhance the affinity of the metal for the oxygen donor sites of anionic ligands,[34] it is of interest to study the effect of such additional ligands on the ligating sites and on the tautomeric conversions of the B_6 vitamins. In this paper we report, for the first time, the syntheses, properties, and X-ray structures of Co(III) and Cu(II) complexes of PN and bpy. The two crystal structures, wherein PN is anionic in one and neutral in the other, reveal that chelation occurs through the 4-(hydroxymethyl) and phenolate groups of the dipolar tautomer in the presence of a ternary ligand as well.

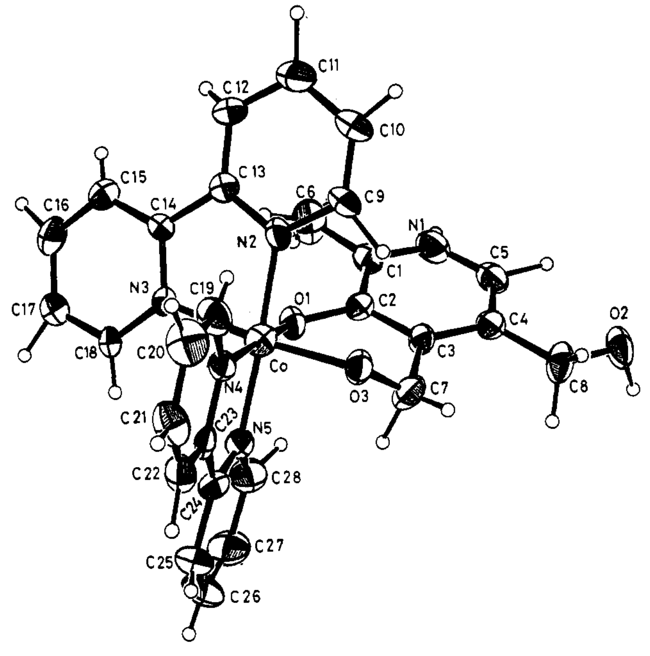

Figure 1. ORTEP drawing of the $[Co(bpy)_2(PN-H)]^{2+}$ cation showing the atom numbering and thermal motion ellipsoids (50% probability level) for non-hydrogen atoms. The hydrogen atoms are represented by circles.

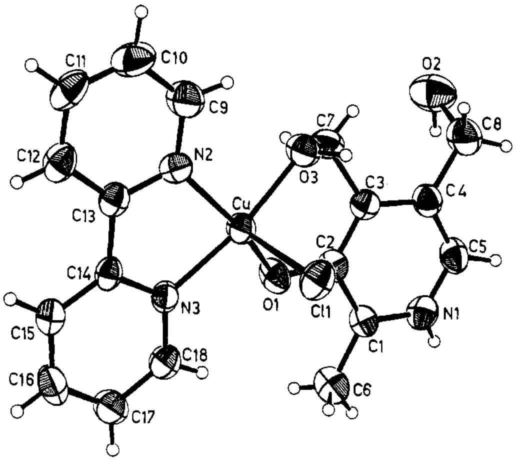

Figure 2. ORTEP drawing of the $[Cu(bpy)(PN)Cl]^{+}$ cation showing the atom numbering and thermal motion ellipsoids (50% probability level) for non-hydrogen atoms. The hydrogen atoms are represented by circles.

Experimental Section

Preparation of (Pyridoxinato)bis(2,2'-bipyridyl)cobalt(III) Perchlorate, $[Co(bpy)_2(PN-H)](ClO_4)_2$. To a mixture of cobalt(II) perchlorate (1 mmol) and bpy (2 mmol) in ethanol (10 mL) was added slowly an aqueous solution of PN (1 mmol in 5 mL). The solution (pH 5.6), initially pink-yellow, later turned dark pink. By controlled slow evaporation, beautiful reddish pink, parallelepiped-shaped crystals separated out after 2 days. The crystals were filtered, washed with ether, and dried under vacuum; yield 82%.

Preparation of Chloro(2,2'-bipyridyl)(pyridoxine)copper(II) Perchlorate Hydrate, $[Cu(bpy)(PN)Cl](ClO_4)\cdot H_2O$. Copper(II) perchlorate (1 mmol) and bpy (1 mmol) were dissolved in a 1:1 water-ethanol mixture (10 mL). To this solution was added an aqueous solution of PN (1 mmol in 5 mL) when the color of the solution changed from blue to green (pH 5.1). By slow controlled evaporation, dark green crystals separated out, which were filtered and dried under vacuum; yield 95%.[35]

Physical Measurements. The electronic spectra of the compounds were recorded with a Unicam SP700A spectrophotometer. The infrared spectra were recorded with a Perkin-Elmer 599 spectrometer on KBr pellets as support in the 4000–250-cm^{-1} spectral range. The ^1H NMR spectrum for $[Co(bpy)_2(PN-H)](ClO_4)_2$ was obtained from a Bruker WH 270 FT spectrometer operating at 270 MHz in D_2O with TSP as

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(18) For atom numbering in anionic PN see structure V. It may be noted that the ring atom numbering in PN (with the methyl group at the 6-position) is the reverse of that followed in PM, PL, or their derivatives (with the methyl group at the 2-position). However, for the sake of uniformity, the labeling of the atoms (Figures 1 and 2) has been retained the same as in our earlier work on the complexes of pyridoxylidene Schiff bases[6] and of PL derivatives.[42c]

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Table I. Summary of Crystal Data Collection

	$[Co(bpy)_2(PN\text{-}H)](ClO_4)_2$	$[Cu(bpy)(PN)Cl]ClO_4 \cdot H_2O$
mol formula	$C_{28}H_{26}Cl_2CoN_5O_{11}$	$C_{18}H_{21}Cl_2CuN_3O_8$
mol wt	738.39	541.44
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	18.900 (3)	12.136 (5)
b, Å	8.764 (1)	13.283 (4)
c, Å	20.041 (2)	7.195 (2)
α, deg	90	96.91 (2)
β, deg	116.05 (1)	91.25 (3)
γ, deg	90	71.63 (3)
V, Å^3	2982.3	1092.6
Z	4	2
$F(000)$	1508	554
ρ(calcd), g/cm^3	1.64	1.64
ρ(obsd), g/cm^{3d}	1.64	1.62
diffractometer	CAD4	Syntex $P2_1$
radiation	Ni-filtered Cu Kα (λ = 1.542 Å)	graphite-monochromated Mo Kα (λ = 0.7107 Å)
temp, K	296	298
reflecns measd	$\pm h,+k,+l$	$\pm h,\pm k,+l$
scan type	$\omega/2\theta$	$\omega/2\theta$
θ range, deg	4–70	2–22.5
scan speed, deg/min	10	2.5–12.5
measd reflecns	5905	2841
obsd unique reflecns	3401 ($F_o > 5\sigma(F_o)$)	2094 ($I > 3\sigma(I)$)
cryst size, mm	~0.44 × 0.28 × 0.05	~0.3 × 0.15 × 0.08
abs coeff, cm^{-1}	30.0	12.8
transmission factors	0.81–1.43^a	0.96–1.04^a
weighting scheme (w)	$[\sigma^2(F_o) + 0.006F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.0001F_o^2]^{-1}$
R^b	0.080	0.042
$R_w{}^c$	0.118	0.051

^{a}Normalized to an average of unity. $^b R = \sum|F_o - |F_c||/\sum F_o$. $^c R_w = [\sum w(F_o - |F_c|)^2/\sum F_o^2]^{1/2}$. ^{d}By flotation in $CHCl_3 + CHBr_3$.

internal standard. The ESR spectrum for $[Cu(bpy)(PN)Cl]ClO_4 \cdot H_2O$ was recorded on a Varian E109 spectrometer. The room-temperature magnetic susceptibilities were measured by the Faraday method using $Hg[Co(CNS)_4]$ as the calibrant.

Collection and Reduction of the X-ray Intensity Data. Details regarding the data collection and processing are presented in Table I. The data were corrected for Lorentz, polarization, and absorption effects.

Solution and Refinement of the Structures. The structures were solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares treatment. All the hydrogen atoms were located from difference electron density maps and their positions and isotropic temperature factors refined in the last three cycles. The shifts in parameters for both compounds in the last cycle was less than 0.1σ. Final residuals R and R_w are 0.080 and 0.118 for $[Co(bpy)_2(PN\text{-}H)](ClO_4)_2$ and 0.042 and 0.051 for $[Cu(bpy)(PN)Cl]ClO_4 \cdot H_2O$. The final difference electron density map for the Co compound revealed no significant electron density except a few peaks less than 0.9 e Å^{-3} at distances 1.4–1.7 Å from the chlorine of one of the perchlorate ions. No peak higher than 0.3 e Å^{-3} was observed in the map for the Cu compound.

Major calculations were performed on a DEC 1090 computer using the SHELX-76 system of programs[36] for Fourier and least-squares calculations and ORTEP-II[37] and PLUTO-78[38] programs for diagrams.[39] The scattering factors for H, C, N, O, and Cl atoms were used as available in the SHELX program, and for Co and Cu they were taken from ref 40 (anomalous dispersion corrections applied). The final atomic coordinates for the compounds are given in Tables II and III.

Results and Discussion

The molecular structures and the atom-labeling schemes of the two compounds $[Co(bpy)_2(PN\text{-}H)](ClO_4)_2$ and $[Cu(bpy)(PN)Cl]ClO_4 \cdot H_2O$ are shown in Figures 1 and 2, respectively. Selected bond distances and angles are presented in Tables IV and V.

Metal Coordination and Chelate Rings. In $[Co(bpy)_2(PN\text{-}H)](ClO_4)_2$, the Co(III) ion has three bidentate ligands in one PN-H and two bpy groups. The coordination geometry is octahedral with phenolic oxygen O(1) and 4-(hydroxymethyl) oxygen O(3) from PN-H and two nitrogens each from two bpy's as the donor atoms. The equatorial plane, containing donors from PN-H, has other donor atoms from different bpy's. The least-squares plane passing through these atoms makes a dihedral angle of 26.8° with that of the pyridine ring of PN-H. The metal–donor atom distances are in the range 1.876–1.985 (6) Å, and the cis bond angles around the metal range between 81.9 and 97.3 (3)°. These values are comparable with those of similar Co(III) complexes.[41] Interestingly, one of the four Co–N bonds, Co–N(3), is significantly longer (1.985 (8) Å) than the other three (~1.93 Å). A notable point is that, among the three equatorial planes of the octahedron, the one involving donors from PN-H is tetrahedrally distorted (deviations ±0.085 Å), whereas the other two are virtually planar (supplementary Table VI).

Cu(II) in $[Cu(bpy)(PN)Cl]ClO_4 \cdot H_2O$ has a distorted-square-pyramidal geometry. O(1) and O(3) of PN and N(2) and N(3) of bpy constitute the square base while a Cl atom occupies the axial site. The equatorial bond lengths, which are in the range 1.928–2.002 (4) Å, are somewhat longer than those observed in pyridoxylidene Schiff base complexes of copper[6,21,26-29] but compare well with those of PM compounds $Cu(PM)_2(NO_3)_2 \cdot H_2O$ and $Cu(PM\text{-}H)_2 \cdot 2H_2O$.[16] The Cu–Cl(1) distance is normal and is in the range observed for the Cu compounds having Cl at the axial site.[26b,42] The cis bond angles in the plane range from 81.3 to 92.1 (2)°, the smallest being that of the five-membered chelate ring. The Cu–Cl(1) bond makes an angle of 3.4° with the normal

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Table II. Fractional Atomic Coordinates (×10^4) for Non-Hydrogen Atoms in $[\mathrm{Co(bpy)_2(PN\text{-}H)}](\mathrm{ClO_4})_2$ with Their Esd's in Parentheses

atom	*x*	*y*	*z*
Co	2487 (1)	287 (1)	874 (1)
N(1)	4615 (4)	−3285 (8)	878 (4)
C(1)	3860 (4)	−3004 (9)	676 (4)
C(2)	3673 (4)	−1876 (9)	1060 (4)
C(3)	4274 (4)	−1043 (9)	1622 (4)
C(4)	5074 (4)	−1421 (9)	1824 (4)
C(5)	5215 (4)	−2559 (10)	1436 (4)
C(6)	3256 (5)	−3918 (12)	51 (6)
C(7)	4043 (4)	192 (10)	2002 (4)
C(8)	5734 (4)	−648 (10)	2454 (5)
O(1)	2909 (3)	−1663 (6)	892 (3)
O(2)	6477 (3)	−1371 (7)	2627 (3)
O(3)	3450 (3)	1167 (6)	1524 (3)
N(2)	2669 (3)	697 (7)	19 (3)
C(9)	3327 (4)	1426 (10)	34 (4)
C(10)	3430 (5)	1562 (12)	−587 (5)
C(11)	2874 (5)	992 (11)	−1266 (5)
C(12)	2192 (4)	311 (10)	−1280 (4)
C(13)	2120 (4)	158 (9)	−636 (4)
C(14)	1461 (4)	−604 (9)	−580 (4)
C(15)	863 (4)	−1354 (11)	−1146 (4)
C(16)	300 (5)	−2094 (11)	−1021 (5)
C(17)	304 (4)	−1963 (10)	−338 (4)
C(18)	904 (4)	−1193 (9)	218 (4)
N(3)	1486 (3)	−554 (7)	104 (3)
N(4)	2001 (3)	2219 (7)	894 (3)
C(19)	1880 (4)	3387 (9)	433 (4)
C(20)	1562 (5)	4736 (11)	521 (5)
C(21)	1388 (4)	4940 (9)	1108 (5)
C(22)	1503 (4)	3745 (10)	1579 (4)
C(23)	1804 (3)	2388 (9)	1464 (4)
C(24)	1923 (4)	1018 (9)	1903 (4)
C(25)	1707 (5)	802 (11)	2473 (4)
C(26)	1840 (6)	−593 (14)	2833 (5)
C(27)	2167 (6)	−1721 (11)	2624 (5)
C(28)	2388 (5)	−1505 (10)	2061 (4)
N(5)	2256 (3)	−158 (7)	1700 (3)
Cl(1)	221 (1)	1910 (3)	3385 (1)
O(4)	160 (5)	2760 (10)	3954 (4)
O(5)	381 (5)	2867 (10)	2894 (4)
O(6)	−466 (4)	1092 (11)	2966 (4)
O(7)	848 (6)	860 (13)	3707 (5)
Cl(2)	5515 (1)	3022 (3)	1050 (1)
O(8)	4937 (6)	3646 (13)	389 (5)
O(9)	6033 (5)	4366 (14)	1285 (7)
O(10)	5132 (6)	2782 (11)	1516 (5)
O(11)	5815 (10)	1806 (14)	868 (11)

Table III. Fractional Atomic Coordinates (×10^4) for Non-Hydrogen Atoms in $[\mathrm{Cu(bpy)(PN)Cl}]\mathrm{ClO_4{\cdot}H_2O}$ with Their Esd's in Parentheses

atom	*x*	*y*	*z*
Cu	3831 (1)	2229 (0)	3956 (1)
N(1)	4335 (4)	5610 (3)	7749 (6)
C(1)	4795 (4)	4568 (4)	7131 (7)
C(2)	4040 (5)	3982 (4)	6552 (7)
C(3)	2842 (5)	4505 (4)	6774 (7)
C(4)	2410 (5)	5602 (4)	7384 (7)
C(5)	3189 (5)	6137 (4)	7876 (8)
C(6)	6057 (5)	4072 (4)	7141 (8)
C(7)	2062 (5)	3818 (4)	6399 (9)
C(8)	1126 (5)	6209 (5)	7551 (9)
O(1)	4499 (3)	2981 (3)	5889 (5)
O(2)	584 (4)	5895 (4)	9037 (6)
O(3)	2256 (3)	3233 (3)	4564 (5)
N(2)	3195 (4)	1096 (3)	2745 (6)
C(9)	2068 (5)	1192 (5)	2471 (8)
C(10)	1727 (6)	344 (5)	1712 (9)
C(11)	2538 (6)	−630 (5)	1240 (9)
C(12)	3692 (6)	−732 (4)	1493 (8)
C(13)	4009 (5)	135 (4)	2271 (7)
C(14)	5206 (5)	108 (4)	2665 (7)
C(15)	6161 (5)	−784 (4)	2258 (8)
C(16)	7238 (5)	−701 (4)	2683 (8)
C(17)	7352 (5)	243 (5)	3536 (8)
C(18)	6374 (5)	1095 (4)	3936 (8)
N(3)	5311 (4)	1040 (3)	3524 (6)
Cl(1)	4036 (1)	3079 (1)	1028 (2)
Cl(2)	661 (1)	7872 (1)	3157 (3)
O(4)	−147 (6)	7396 (6)	3554 (11)
O(5)	1441 (6)	7934 (6)	4585 (10)
O(6)	1370 (7)	7296 (7)	1679 (11)
O(7)	121 (6)	8840 (6)	2627 (15)
O(W1)	1314 (5)	4580 (5)	2300 (9)

Table IV. Selected Bond Distances (Å) and Angles (deg) Involving Non-Hydrogen Atoms in $[\mathrm{Co(bpy)_2(PN\text{-}H)}](\mathrm{ClO_4})_2$ with Their Esd's in Parentheses

Co–O(1)	1.879 (6)	C(3)–C(7)	1.495 (11)
Co–O(3)	1.876 (6)	C(4)–C(5)	1.361 (11)
Co–N(2)	1.925 (6)	C(4)–C(8)	1.492 (12)
Co–N(3)	1.985 (6)	C(7)–O(3)	1.401 (10)
Co–N(4)	1.935 (6)	C(8)–O(2)	1.437 (11)
Co–N(5)	1.928 (6)	Cl(1)–O(4)	1.407 (9)
N(1)–C(1)	1.324 (12)	Cl(1)–O(5)	1.424 (9)
N(1)–C(5)	1.352 (11)	Cl(1)–O(6)	1.396 (9)
C(1)–C(2)	1.391 (11)	Cl(1)–O(7)	1.413 (12)
C(1)–C(6)	1.501 (13)	Cl(2)–O(8)	1.406 (10)
C(2)–C(3)	1.403 (11)	Cl(2)–O(9)	1.471 (12)
C(2)–O(1)	1.345 (10)	Cl(2)–O(10)	1.427 (11)
C(3)–C(4)	1.421 (12)	Cl(2)–O(11)	1.331 (16)

O(1)–Co–O(3)	95.0 (3)	C(3)–C(2)–O(1)	122.1 (7)
O(1)–Co–N(2)	86.9 (3)	C(2)–C(3)–C(4)	119.5 (7)
O(1)–Co–N(3)	85.9 (3)	C(2)–C(3)–C(7)	118.1 (7)
O(1)–Co–N(4)	175.2 (3)	C(4)–C(3)–C(7)	122.4 (7)
O(1)–Co–N(5)	93.1 (3)	C(3)–C(4)–C(5)	117.3 (7)
O(3)–Co–N(2)	92.5 (3)	C(3)–C(4)–C(8)	121.7 (7)
O(3)–Co–N(3)	174.2 (3)	C(5)–C(4)–C(8)	121.0 (7)
O(3)–Co–N(4)	87.2 (3)	N(1)–C(5)–C(4)	120.9 (8)
O(3)–Co–N(5)	90.2 (3)	C(3)–C(7)–O(3)	114.7 (7)
N(2)–Co–N(3)	81.9 (3)	C(4)–C(8)–O(2)	111.6 (7)
N(2)–Co–N(4)	97.3 (3)	Co–O(1)–C(2)	122.1 (5)
N(2)–Co–N(5)	177.3 (3)	Co–O(3)–C(7)	117.7 (5)
N(3)–Co–N(4)	92.4 (3)	Co–N(2)–C(9)	125.2 (5)
N(3)–Co–N(5)	95.5 (3)	Co–N(2)–C(13)	116.0 (5)
N(4)–Co–N(5)	82.6 (3)	Co–N(3)–C(14)	113.4 (5)
C(1)–N(1)–C(5)	124.4 (7)	Co–N(3)–C(18)	126.5 (5)
N(1)–C(1)–C(2)	117.6 (7)	Co–N(4)–C(19)	126.7 (5)
N(1)–C(1)–C(6)	118.6 (8)	Co–N(4)–C(23)	114.9 (5)
C(2)–C(1)–C(6)	123.8 (8)	Co–N(5)–C(24)	114.4 (5)
C(1)–C(2)–C(3)	120.1 (7)	Co–N(5)–C(28)	125.4 (5)
C(1)–C(2)–O(1)	117.8 (7)		

to the square plane. The four basal atoms show small but significant tetrahedral deviations (−0.092 to 0.130 (4) Å) from the least-squares plane through these atoms. As in $[\mathrm{Co(bpy)_2(PN\text{-}H)}](\mathrm{ClO_4})_2$, this plane is not coplanar with the plane through the pyridine ring of PN, the two making a dihedral angle of 18.0°.

There are two five-membered rings and one six-membered chelate ring in $[\mathrm{Co(bpy)_2(PN\text{-}H)}](\mathrm{ClO_4})_2$ and one each in the case of $[\mathrm{Cu(bpy)(PN)Cl}]\mathrm{ClO_4{\cdot}H_2O}$. The chelate ring bites are 2.768, 2.562, and 2.549 Å for the six-membered and two five-membered rings, respectively, in the Co compound and 2.796 and 2.596 Å in the Cu compound. The five-membered chelate rings are nearly planar as expected. However, in the case of six-membered chelate rings, torsion angles and asymmetry parameters[43] (supplementary Table V) indicate that the ring assumes a sofa conformation in $[\mathrm{Cu(bpy)(PN)Cl}]\mathrm{ClO_4{\cdot}H_2O}$, whereas in $[\mathrm{Co(bpy)_2(PN\text{-}H)}](\mathrm{ClO_4})_2$ the conformation is between boat and sofa. The base of the boat involves the atoms C(2), C(3), Co, and O(3). Different conformations, e.g., sofa[6] and half-chair,[29] have been observed for such six-membered chelate rings of related compounds.

Pyridoxine and Bipyridyl Ligands. All the vitamin B_6 constituents are known to exist in various tautomeric forms. The known structures of vitamin B_6 compounds[44] and their metal complexes[6,15–17,19–22,25–30] can be grouped into four categories: those

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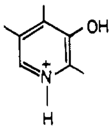
(43) Duax, W. L.; Weeks, C. M.; Rohrer, D. C. *Top. Stereochem.* **1976**, *9*, 279–286.

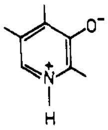
Table V. Selected Bond Distances (Å) and Angles (deg) Involving Non-Hydrogen Atoms in [Cu(bpy)(PN)Cl]$ClO_4 \cdot H_2O$ with Their Esd's in Parentheses

Cu–O(1)	1.928 (4)	C(3)–C(4)	1.402 (7)
Cu–O(3)	1.978 (4)	C(3)–C(7)	1.509 (8)
Cu–N(2)	2.002 (4)	C(4)–C(5)	1.368 (8)
Cu–N(3)	1.984 (4)	C(4)–C(8)	1.511 (9)
Cu–Cl(1)	2.559 (2)	C(7)–O(3)	1.433 (7)
N(1)–C(1)	1.342 (6)	C(8)–O(2)	1.436 (8)
N(1)–C(5)	1.345 (8)	Cl(2)–O(4)	1.375 (8)
C(1)–C(2)	1.405 (8)	Cl(2)–O(5)	1.394 (8)
C(1)–C(6)	1.465 (8)	Cl(2)–O(6)	1.374 (9)
C(2)–C(3)	1.403 (9)	Cl(2)–O(7)	1.343 (8)
C(2)–O(1)	1.302 (6)		
O(1)–Cu–O(3)	91.4 (2)	C(3)–C(2)–O(1)	124.3 (5)
O(1)–Cu–N(2)	157.8 (2)	C(2)–C(3)–C(4)	121.0 (5)
O(1)–Cu–N(3)	92.1 (2)	C(2)–C(3)–C(7)	116.5 (5)
O(1)–Cu–Cl(1)	103.4 (1)	C(4)–C(3)–C(7)	122.5 (5)
O(3)–Cu–N(2)	92.0 (2)	C(3)–C(4)–C(5)	118.3 (5)
O(3)–Cu–N(3)	170.1 (2)	C(3)–C(4)–C(8)	122.8 (5)
O(3)–Cu–Cl(1)	93.2 (1)	C(5)–C(4)–C(8)	119.0 (5)
N(2)–Cu–N(3)	81.3 (2)	N(1)–C(5)–C(4)	119.9 (5)
N(2)–Cu–Cl(1)	98.3 (1)	C(3)–C(7)–O(3)	112.0 (5)
N(3)–Cu–Cl(1)	95.0 (1)	C(4)–C(8)–O(2)	111.5 (5)
C(1)–N(1)–C(5)	124.2 (5)	Cu–O(1)–C(2)	124.8 (3)
N(1)–C(1)–C(2)	118.6 (5)	Cu–O(3)–C(7)	117.3 (3)
N(1)–C(1)–C(6)	119.2 (5)	Cu–N(2)–C(9)	126.5 (4)
C(2)–C(1)–C(6)	122.2 (5)	Cu–N(2)–C(13)	114.3 (4)
C(1)–C(2)–C(3)	117.8 (5)	Cu–N(3)–C(14)	115.1 (4)
C(1)–C(2)–O(1)	117.9 (5)	Cu–N(3)–C(18)	126.1 (4)

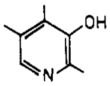
containing cation I, neutral zwitterion II, neutral nondipolar form III, and anion IV. Structures containing cation I[44a–c] have a phenolic C–O distance of ~1.34 Å. Deprotonation at phenolic O to give zwitterion II results in shortening of the C–O bond by ~0.05 Å, while the angle at nitrogen (~124°) remains unchanged.[6,15–17,19,21,22,25,26,44d,e] In the neutral form III, the C–O bond length is unchanged but the angle at nitrogen decreases to ~120°.[44f] In the structural entity IV, the C–O distance is ~1.30 Å and the angle at nitrogen is ~119°.[16,20,27–30] In most of the known structures of metal–vitamin B_6 complexes, the ligand is of the type II. PN can exist in two tautomeric forms, with either pyridine nitrogen or phenolic oxygen being protonated, corresponding to the moieties II and III, respectively.



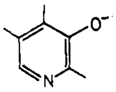
I



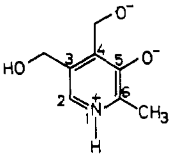
II



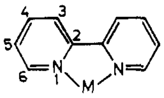
III



IV



V



VI

Table VI. Possible Hydrogen Bonds[a]

X–H···Y	X–H, Å	X···Y, Å	H···Y, Å	X–H–Y, deg
		[Co(bpy)$_2$(PN-H)]$(ClO_4)_2$		
N(1)–H(1)···O(8)^{i}	0.77 (12)	3.02 (1)	2.25 (12)	172 (14)
O(2)–H(10)···O(3)^{ii}	1.15 (11)	2.714 (8)	1.67 (12)	148 (11)
		[Cu(bpy)(PN)Cl]$ClO_4 \cdot H_2O$		
N(1)–H(1)···Cl(1)^{iii}	0.78 (10)	3.072 (5)	2.31 (10)	166 (10)
O(2)–H(10)···O(6)^{iv}	1.05 (5)	2.86 (1)	1.98 (5)	139 (4)
O(3)–H(11)···O(W1)	1.04 (11)	2.549 (7)	1.55 (12)	158 (13)
O(W1)–H(21)···O(2)^{v}	0.80 (14)	2.703 (8)	2.08 (15)	135 (14)

[a] Symmetry superscripts: (i) $x, -1 + y, z$; (ii) $1 - x, -^1/_2 + y, ^1/_2 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $x, y, 1 + z$; (v) $-x, 1 - y, 1 - z$.

In [Cu(bpy)(PN)Cl]$ClO_4 \cdot H_2O$, the C(2)–O(1) bond distance, 1.302 (6) Å, and the angle C(1)–N(1)–C(5), 124.2 (5)°, are normal.[6,15–17,19,21,22,25,26] However, in [Co(bpy)$_2$(PN-H)]$(ClO_4)_2$, while the angle at the pyridine nitrogen is 124.4 (7)°, indicating protonation at this site,[45] the C(2)–O(1) distance, 1.345 (10) Å, is very close to C–O distances found in free B_6 vitamins[44a–c] wherein O is protonated;[46] however, it is shorter than that in free PN (1.374 (4) Å).[44f] This lengthening can be explained in terms of a decrease in partial double-bond character due to the coordination of O(1) to a strongly acidic Co(III). The foregoing discussion, together with the locations of the hydrogen atoms, shows that the PN ligand occurs as the neutral tautomer II in [Cu(bpy)(PN)Cl]$ClO_4 \cdot H_2O$. However, in [Co(bpy)$_2$(PN-H)]$(ClO_4)_2$, a new anionic species V is observed where the 4-(hydroxymethyl) group is deprotonated.[47] In the latter case, the alcoholic group has apparently become more acidic on complexation when compared to the case for the free ligand, on account of the higher charge on Co(III), resulting in easy removal of the proton.[48] Such a situation has also been observed in the case of Co(III)–amino alcohol systems where coordinated alcoholate could be protonated only under highly acidic conditions.[41c] On the other hand, in [Cu(bpy)(PN)Cl]$ClO_4 \cdot H_2O$, due to the lower charge on Cu(II), alcoholic O has not been rendered so acidic as to lose a proton. Furthermore, the octahedral environment around Co(III) with short metal-donor distances may also have a role in the removal of the hydroxymethyl proton.

In the case of Co(III) complexes of amino alcohols[41b,c] it has been observed that the Co–O distances, 1.932 and 1.968 Å in the protonated compound, reduce to 1.877 and 1.900 Å in the deprotonated compoud. In [Co(bpy)$_2$(PN-H)]$(ClO_4)_2$ also, similar short Co–O distances (Co–O(1) = 1.879 (6); Co–O(3) = 1.876 (6) Å) are indicative of the deprotonated negatively charged oxygens. On the other hand, in [Cu(bpy)(PN)Cl]$ClO_4 \cdot H_2O$ the differences in Cu–O(1) and Cu–O(3) distances may be noted. The effect of negative charge on O(3) in the Co complex is further manifested in the shortened C(7)–O(3) bond length (1.401 (10)

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(44) (a) Giordano, F.; Mazzarella, L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1971**, *B27*, 128. (b) Fujiwara, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 863. (c) Bacon, G. E.; Plant, J. S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1130. (d) Longo, J.; Richardson, M. F. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2456. (e) Rao, S. P. S.; Poojary, M. D.; Manohar, H. *Curr. Sci.* **1982**, *51*, 410. (f) Longo, J.; Franklin, K. J.; Richardson, M. F. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 2721.

(45) Singh, C. *Acta Crystallogr.* **1965**, *19*, 861.

(46) A similar C–O distance (1.331 (3) Å) is also observed in the anionic moiety of Cu(PM-H)$_2 \cdot 2H_2O$.[16]

(47) The diamagnetism of [Co(bpy)$_2$(PN-H)]$(ClO_4)_2$, the absence of an ESR signal, and the nature of its NMR spectrum (absence of shift and broadening due to paramagnetic effect) indicate that the metal ion is in the +3 state. As there are only two perchlorate ions, the pyridoxine group has to be anionic for charge neutrality. PN is a zwitterion with the negative charge residing on phenolic O and positive charge on protonated pyridine N. There is no peak of any significant intensity near O(3) in the final difference electron density map, indicating the O(3) atom to be deprotonated. Further support to this conclusion comes from the hydrogen-bonding pattern (*vide infra*).

(48) In fact, pH-metric titration of 2.6×10^{-4} M [Co(bpy)$_2$(PN-H)]$(ClO_4)_2$ in the pH range 3–11 shows that there are two deprotonation steps. In the first step corresponding to deprotonation at phenolic O (pH range 4–6.5; $pK_a \approx 4.45$) 1 mol of sodium hydroxide/mol of the compound is consumed, whereas in the second step (pH range 6.5–10; $pK_a = 6.85$), which is quite steep when compared to that of free PN, 2 mol of the base/mol of the compound is consumed. This indicates that two protons [on pyridinium N and 4-(hydroxymethyl) O], having nearly the same pK_a, are released together during the second step of the titration. Thus, there are shifts in the pK_a's of the pyridine N (from its normal value of 8.75 in free PN) and of hydroxymethyl O (for primary alcohols pK_a is of the order of 18[49]) to a value of 6.85 upon coordination of the ligand to Co(III).

(49) March, J. "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", 2nd ed.; McGraw-Hill: New York, 1977; pp 227–229.

Table VII. Room-Temperature Electronic and Infrared (cm^{-1}) Spectra and Magnetic Moments (μ_B)

	$[Co(bpy)_2(PN\text{-}H)](ClO_4)_2$	$[Cu(bpy)(PN)Cl]ClO_4 \cdot H_2O$
d–d bands ($\times 10^{-3}$)	19.0	14.9
intraligand bands ($\times 10^{-3}$)	31.7, 33.1, 40.8, 46.1	30.3, 32.4, 33.6, 41.3, 47.6
ν(aromatic)	1600	1610
ν(phenol C–O)	1515	1500
$\nu(ClO_4)$	1100 (broad)	1100 (broad)
μ_{eff}	diamag	1.85

Å) and increased bond angle around C(7) [C(3)–C(7)–O(3) = 114.7 (7)°] as compared to the values in the Cu complex [C(7)–O(3) = 1.433 (7) Å; C(3)–C(7)–O(3) = 112.0 (5)°] and those corresponding to the uncoordinated hydroxymethyl groups of both complexes (for these values, see Tables IV and V).[50] These small but significant deviations may be attributed to a slight double-bond character that may be associated with the C(7)–O(3) bond due to the negative charge on O(3). Other bond distances and angles in PN and PN-H are unexceptional.

The pyridine rings are planar. The bpy moieties have normal bond lengths and angles as observed in similar compounds.[42a,51] The individual rings of each bpy are planar. However, the two rings of a molecule take their customary tilt, the dihedral angle between the planes of the rings being 5.33 and 6.26° in the Co compound and 2.80° in the Cu compound.

Perchlorate Groups. While the only perchlorate group in $[Cu(bpy)(PN)Cl]ClO_4 \cdot H_2O$ and one of the two in $[Co(bpy)_2(PN\text{-}H)](ClO_4)_2$ are normal, the second perchlorate group of the latter involving Cl(2) is highly unsymmetrical (Cl–O bond lengths 1.33–1.47 (2) Å and bond angles 97.0–117.4 (9)°). Furthermore, temperature factors of O(11), in particular, are very high, suggesting possible disorder for the group.

Molecular Packing and Hydrogen Bonding. The pyridine N is involved in hydrogen bond formation with O(8) of a perchlorate group in the Co compound and coordinated Cl(1) of a centrosymmetrically related molecule in the Cu compound. Hydroxymethyl oxygen O(3) forms a hydrogen bond with O(2) of a screw-related molecule in the Co compound and water oxygen O(W1) in the other. However, it is a proton acceptor in the former and a donor in the latter, another indication of deprotonation at O(3) in the Co compound. O(2) of the Cu compound is involved in two hydrogen bonds, one with O(6) of the perchlorate group and the other with the lattice water O(W1) (Table VI). The packing in this compound is further stabilized by partial stacking of bpy groups of centrosymmetrically related molecules at a distance of ~3.55 Å.

Magnetic and Spectral Properties. The diamagnetism of $[Co(bpy)_2(PN\text{-}H)](ClO_4)_2$ is in agreement with the low-spin d^6 system in an octahedral field, whereas the room-temperature magnetic moment of $[Cu(bpy)(PN)Cl]ClO_4 \cdot H_2O$ is typical of magnetically dilute complexes. The room-temperature EPR parameters ($g_{\parallel} = 2.227$, $g_{\perp} = 2.069$) of the polycrystalline Cu compound and its electronic spectrum in aqueous solution, which shows an absorption maximum at 14925 cm^{-1}, are comparable with those reported for most of the square-pyramidal copper(II) complexes.[52] The electronic spectrum of the Co compound (aqueous solution) shows a broad peak at 19010 cm^{-1}, typical of octahedral Co(III).[41a,b,53] The UV region of the electronic spectra of both the complexes is characterized by the usual intraligand bands (Table VII).[13,23]

In the infrared spectra of both the compounds, the peaks characteristic of coordinated bpy are observed at 1600, 1490, 1440, and 620 cm^{-1}. A weak band at ~1560 cm^{-1} probably corresponds to protonated pyridinium nitrogen.[54] A band of medium intensity at ~1505 cm^{-1} is characteristic of coordinated phenolic $C\text{–}O^-$ stretching observed for many of the vitamin B_6 complexes.[9,23,28] No peak can be assigned unambiguously to metal–ligand vibrations in the region below 600 cm^{-1}, since the ligands themselves have several absorptions in this region.

The ^1H NMR spectrum of $[Co(bpy)_2(PN\text{-}H)](ClO_4)_2$ recorded in D_2O showed clearly the nonequivalence of protons of both PN-H and bpy ligands. The protons of $4\text{-}CH_2O^-$ of PN-H exhibit a typical AB pattern (δ 3.69, J = 15.3 Hz). The other proton signals of PN-H appear at δ 1.80 for $-CH_3$ and δ 7.85 for the ring hydrogen. The signal due to $-CH_2-$ at C(4) is probably buried in that of water. The protons of the two bpy's are nonequivalent, and the signals appear as distinct doublets or triplets in the normal range in which coordinated bpy protons resonate.[55] In fact, 13 proton environments out of a possible 16 are clearly observed.[56]

Conclusions

It has been postulated that, in aqueous solution, PN exists in the zwitterionic form II.[57-59] However, PN is converted to the nondipolar form III in dioxane and alcohols.[59] In the crystalline state also, free PN exists in the nondipolar form.[44f] The crystal packing apparently stabilizes this form so that a tautomeric change occurs in PN even as it crystallizes from aqueous solution. Tautomeric changes during crystallization as free entities or as complexes of metals are common to all B_6 vitamins. It has been pointed out that a judicious choice of solvent might allow one to observe complexation of various tautomeric forms of the vitamins, perhaps even accompanied by a change in ligating sites.[54] For example, in the pyridoxine–Cu(II) system, the ring nitrogen, which is protonated in aqueous solution, becomes an important donor site in H_2O/Me_2SO mixed solvent.[10] In the present case, as pointed out earlier, the charge on the metal ion, Co(III), and possibly the coordination environment have caused the deprotonation of the $4\text{-}CH_2OH$ group, thus converting the dipolar PN into an anionic moiety. In addition, Co(II) with bpy ligands is known to form dioxygen complexes,[60] and the involvement of such a species in the deprotonation of PN may not be ruled out. Apparently, these factors also have a significant role in bringing about tautomeric changes in vitamins and in causing them to become charged species. This kind of behavior is especially relevant to enzymic systems since the microenvironment of the vitamins will be very different from that in bulk aqueous solution. A further point is that attempts to crystallize binary compounds of PN with different metal ions (Co(II), Ni(II), Cu(II), Zn(II)) were not successful. The fact that in the presence of an additional ligand, bpy, ternary complexes crystallized out easily emphasizes the role of the ternary ligand in stabilizing the complexes of PN.

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(50) In the only other PN complex, $Cd(PN)Cl_2$, whose structure is solved[15] also, C(7)–O(3) is 1.468 Å and C(3)–C(7)–O(3) is 107.7°.

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(56) Tentative NMR assignments are listed below (δ (no. of protons, J (in Hz))): H3, H6 (doublets) 9.14 (1, 5.5), 8.77 (1, 7.7), 8.69 (1, 5.5), 8.63 (4, 8.1), 8.58 (1, 7.7); H4, H5 (triplets) 8.37 (1, 9.9), 8.30 (1, 8.1), 8.22 (1, 6.8), 8.08 (1, 7.0), 6.67 (1, 5.1), 7.65 (1, 7.0), 7.52 (1, 6.6), 7.35 (1, 5.1). For numbering of bpy protons, see structure VI.

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Registry No. $[Co(bpy)_2(PN\text{-}H)](ClO_4)_2$, 100229-36-5; $[Cu(bpy)(PN)Cl](ClO_4)\cdot H_2O$, 100229-39-8.

Supplementary Material Available: Listings of thermal parameters, positional parameters of the hydrogen atoms, selected torsion angles and asymmetry parameters, least-squares planes, bond lengths and angles in bpy moieties, and observed and calculated structure factors and packing diagrams (Figures 3 and 4) (48 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Texas at Austin, Austin, Texas 78712

Reactivity of Phosphenium Ions toward 1,3- and 1,4-Dienes

A. H. Cowley,* R. A. Kemp, J. G. Lasch, N. C. Norman, C. A. Stewart, B. R. Whittlesey, and T. C. Wright

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The phosphenium ions $[(i\text{-}Pr_2N)_2P]^+$ (**1**), $[(Me_2N)_2P]^+$ (**7**), and $[(i\text{-}Pr_2N)ClP]^+$ (**10**) react with a variety of 1,3-dienes to afford the corresponding 3-phospholenium (1-phosphacyclopent-3-enium) cations. The product of the reaction of **1** with 2,3-dimethyl-1,3-butadiene (**2**) was characterized by X-ray crystallography. Compound **2** crystallizes in the space group $P2_1/c$ (No. 14) with $Z = 4$, $a = 9.005$ (2) Å, $b = 16.134$ (4) Å, $c = 18.271$ (2) Å, and $\beta = 96.94$ (1)°. The product of the reaction of **7** with isoprene (**11**) was also characterized by X-ray crystallography. Compound **11** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 15.921$ (2) Å, $b = 7.903$ (12) Å, $c = 32.142$ (4) Å, and $\beta = 102.46$ (1)°. The reactivity of **10** toward the 1,4-dienes, penta-1,4-diene and cyclohexa-1,4-diene, was also investigated. The product of the penta-1,4-diene reaction (**15a**) was characterized by X-ray crystallography. Compound **15a** crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19) with $a = 8.309$ (4) Å, $b = 15.264$ (2) Å, and $c = 15.936$ (2) Å. Mechanistic aspects of these reactions are discussed from the standpoint of product distribution.

Introduction

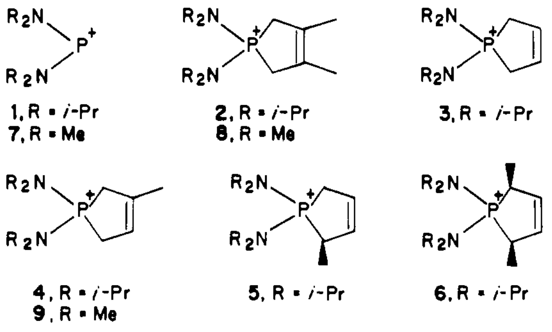
In the singlet state,[1] phosphenium ions (R_2P^+) feature two bond pairs and one lone pair of electrons at the cationic center. As a consequence, these six-electron species are expected to resemble electrophilic carbenoids in their chemical properties.[2] Bearing this parallel in mind, we are investigating the reactivity of phosphenium ions toward a variety of unsaturated organic substrates.

Phosphenium ions have, in fact, been postulated as intermediates in the McCormack reaction of dichlorophosphines with 1,3-dienes.[3] A somewhat stronger case for their intermediacy stems from the fact that complexes of the type $RPX_2\cdot AlX_3$ (R = Me, Ph; X = Cl, Br) are reactive toward 1,4-dienes.[4] In view of the foregoing, it was of interest to determine whether stabilized phosphenium ions would react with 1,3- and/or 1,4-dienes. Moreover, as recognized by SooHoo and Baxter[5] and ourselves,[6] the diene/phosphenium ion reaction represents a potentially useful and convenient synthetic route to phosphorus heterocycles.

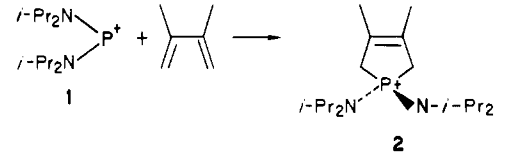
Results and Discussion

(i) Reaction of Phosphenium Ions with 1,3-Dienes: Synthesis, Structure, and Spectroscopic Properties of 3-Phospholenium Ions.

Chart I



Initial studies on the reactivity of phosphenium ions toward dienes centered on the reaction of $[(i\text{-}Pr_2N)_2P][AlCl_4]$ (**1**) with 2,3-dimethyl-1,3-butadiene. After a reaction time of 3 h at room temperature, a complete and quantitative conversion of **1** to **2** occurred as evidenced by ^{31}P NMR spectroscopy. The ^1H, ^{13}C, and ^{31}P NMR spectra of **2** (Table I) were consistent with its formulation as a 3-phospholenium (1-phosphacyclopent-3-enium) cation. This structure assignment was confirmed by an X-ray diffraction study of the tetrachloroaluminate salt of **2**, the results of which are illustrated in Figures 1 and 2 along with the atom-numbering schemes. Tables of bond lengths, bond angles, and atomic positional parameters are presented in Tables II–IV, while pertinent crystallographic data are collected in Table V.



The phosphacyclopentene ring of **2** adopts an envelope conformation for which the "hinge" is defined by the C1–C4 vector with the angle between the planes P1, C1, C4 and C1, C2, C3, C4 being 22.4°. The C–C bond lengths within the ring clearly demonstrate that the double bond is localized between C2 and C3 (1.319 (5) Å), which also carry the two methyl groups. The remaining carbon–carbon distances (average 1.512 (5) Å) cor-

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