trogen atoms. The coordination environment of each copper atom is spacious and, in contrast to the halide analogues,[9-11] the substituents on the pyridine appear to play little role in determining the structural details beyond considerations of crystal packing and polymer conformation, as discussed below. (In **7**, however, it is of interest to note that Cu-S is short (2.290 (4) Å), paralleled by increases in Cu-N(a,b1) to >2.1 Å. Although this may be a consequence of different electronic properties of the quinoline, S-Cu-N(b1) is unusually large and the influence of steric considerations cannot be totally discounted.) Cu-S-C is remarkably constant, with a range of 100.3 (5) (**4**)-105.4 (6)° (**5**). Thiocyanate geometries are as expected, as are those of the pyridine bases. Angular asymmetries at the coordinated nitrogen atoms are found in the cases of **1**, **3**, **6**, and **7**, where the base has a 2-substituent. The structure of **7** is isomorphous with that of its silver(I) analogue, the only 1:2 Ag(SCN):nitrogen base adduct thus far characterized. In the latter Ag-S is 2.495 (4) Å, with Ag-N(SCN) = 2.332 (5) Å and Ag-N(base) = 2.364 (3), 2.361 (3) Å. The metal-sulfur distance has increased by 0.20$_5$ Å on passing from copper(I) to silver(I), while the metal-nitrogen distances have increased by 0.33 Å in the case of the thiocyanate and 0.25 Å in the case of the base nitrogens, indicative of a strengthening of the metal-sulfur bond at the expense of the metal-nitrogen bonds (thiocyanate in particular). This is equivocably supported by the changes in angular geometry: S-Ag-N(thiocyanate, bases) = 119.6 (1), 109.2 (1), 122.3 (1)°; N(thiocyanate)-Ag-N(bases) = 95.9 (1) 98.3 (1)°; N(base-Ag-N(base = 108.0 (1)°. The Ag-S-C value is not significantly different from that in the copper(I) analogue, being 104.4 (1)°, but C-N-Ag, reflecting the increase in Ag-N(SCN), is greatly diminished, to 142.9 (4)°.

The role of the ligand in determining crystal packing and polymer conformation in **3**-**7** is of interest. All polymers are one-dimensional and may be considered as derivative of the "split-stair" polymer found in the 1:1 adduct of CuI with 2,4,6-collidine or acridine.[10] Consideration of the figures shows that in **3** (and **7**)[2] the generating element of the polymer is a 2_1 screw axis, so that the polymer takes on the aspect of a helix or "spiral" with copper atoms at every half-turn and the ligand planes lying quasi-parallel to the generating axis. We note that the base in each case has the common feature of the presence of a 2-substituent in the pyridine ring. By contrast, in **4** and **5**, where this substituent is absent, the polymer takes on a different aspect, having quasi-*m* symmetry in each case with a planar Cu-(SCN)Cu array (σ = 0.003 (**3**), 0.016 Å (**4**)) and the base nitrogen atoms disposed to either side (δN-(1a,b): 1.68, −1.71 Å (**3**); −1.56, 1.80 Å (**4**)). The polymer axis in each case is parallel to monoclinic *b*. In the more symmetrical of these complexes, **4**, H(2) and H(6) of each ligand are comfortably disposed relative to the polymer plane (H(2a)···H(2b), N(1 − *y*) 3.220 (**3**), 3.284 Å (**4**); H(6a)···H-(6b), C 2.767 (**3**), 2.825 Å (**4**)) a relationship that presumably becomes much more strained with the adoption of a 2-substituent, resulting in the helical conformation. It has been noted elsewhere[11] that the 1:1 adducts of CuCl and CuBr with pyridine result in the stair polymer lying in a $P2_1$ unit cell, while in the case of the iodide analogue the cell volume is doubled as the array passes to $P2_1/c$. It is of interest to note in the present system that a somewhat similar occurrence is found: in **5** the unit cell symmetry is $P2_1$, while in **4**, the cell volume is doubled on passing to $P2_1/c$. **6** is unique in having two similar but independent polymer strings packed pairwise in the structure, resulting in a further cell doubling. The two strands differ in the respect of substituent dispositions. In contradiction of the above tentative classification, **6**, although having a planar spine, also contains a base with a 2-substituent.

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Registry No. **1**, 63610-86-6; **2**, 63610-93-5; **3**, 92126-90-4; **4**, 92126-92-6; **5**, 92126-94-8; **6**, 92126-96-0; **7**, 92126-98-2.

Supplementary Material Available: Listings of structure factor amplitudes, non-hydrogen thermal and hydrogen positional and thermal parameters, and ligand geometries and planes and unit cell projections (61 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie Minérale Moléculaire, Equipe de Recherche Associée au CNRS,
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Molecular and Crystal Structure of an Open Cyclamphosphorane Adduct: Cyclamphosphane-Bis(borane)

JEAN-MARC DUPART,[1a] ANDRE GRAND,[1b] SIMONNE PACE,[1a] and JEAN G. RIESS*[1a]

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The first X-ray structure determination of an "open tautomeric form" derivative of a tetracyclic tetraaminophosphorane, cyclamphosphane-bis(borane), $C_{10}H_{21}N_4P\cdot 2BH_3$ (**5**), is reported. **5** crystallized in the monoclinic space group $P2_1/c$ with a = 12.538 (1) Å, b = 9.835 (1) Å, c = 13.263 (1) Å, β = 114.19 (1)°, and Z = 4. The borane groups are coordinated to the P and N atoms, confirming the NMR data in solution, which pointed to the presence of only one of the two possible diastereoisomers; this has now been identified as **5'**, in which the P-B and N-B bonds are oriented trans to each other with respect to the molecule's mean plane. The P-B bond length (1.858 (5) Å) and N-B bond length (1.619 (6) Å) are in the usual ranges. There is no linear correlation between the sum ($\sum N$) of the bond angles around the three tertiary nitrogen atoms (N1, N2, and N3) and the three corresponding P-N bond lengths. A very short P-N2 bond (1.653 (4) Å) is found, in spite of the distinctly pyramidal geometry of the N2 atom ($\sum N2$ = 341.6 ± 3.0°). The five- and six-membered rings adopt the low-energy "envelope" and "chair" conformations, indicating the absence of noticeable constraints in the polycyclic structure. The results presented in this paper are expected to be relevant to most open tautomeric forms of the tetracyclic tetraaminophosphoranes, whether they are uncomplexed or act as mono- or bidentate ligands toward Lewis acids.

Cyclamphosphorane[2] is known to exist in solution as an equilibrium mixture of the closed phosphorane and the open phosphane tautomers, **1a** (80%) and **1b** (20%), respectively (in toluene). It has recently been shown that under the action

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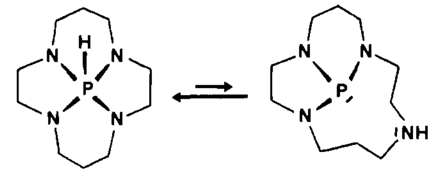
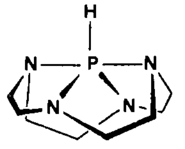

1a (80%) 1b (20%)

of diverse transition-metal complexes, i.e. (η^5-C_5H_5)Mo($CO)_3Cl$, $Fe(CO)_2(NO)_2$, or $[Rh(CO)_2Cl]_2$,[3] this equilibrium can be totally shifted to the right to give phosphorus-bound, or phosphorus- and nitrogen-bound, adducts of the open form **1b**, in which the two donor sites appear to behave independently. Similar behavior was observed when bicyclic aminophosphoranes having a P–H bond were allowed to react with transition-metal derivatives or with diborane.[4] This strongly contrasts with the behavior of cyclenphosphorane **2**, which,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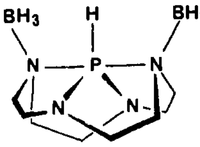
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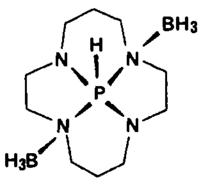
under the action of diborane, did not give adducts of the open-form tautomer.[5] Instead, it was found that two BH_3 groups could be coordinated on two of the phosphorus-bonded nitrogen atoms, with retention of the closed phosphorane structure **3**.

It was therefore of interest to investigate the behavior of cyclamphosphorane toward diborane. Preliminary results[5] have revealed that the reaction is more complex with **1** than with **2** and that a mixture was obtained in which the bisadducts of both the closed (**4**) and the open (**5**) tautomeric forms were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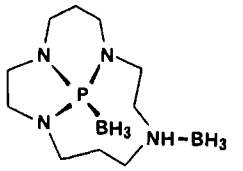
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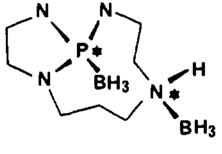
present along with other, still unidentified, products. In a typical experiment, adducts **4** and **5** were isolated in 40 and 15% yields, respectively.

Cyclamphosphane–bis(borane) (**5**) may a priori exist in two diastereoisomeric forms, **5′** and **5″**, since there are two independent chiral centers in the molecule, but all the spectral data point, within the limits of detection, to the presence of only one of these isomers; however, these data do not permit the establishment of which one it is.


5′ (*R,S;S,R*)

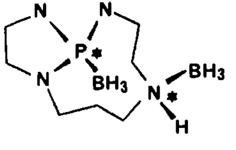

5″ (*R,R;S,S*)

Table I. Crystallographic Data for $C_{10}H_{21}N_4P\cdot 2BH_3$

$C_{10}H_{27}B_2N_4P$
fw = 255.95
space group: $P2_1/c$
$a = 12.538$ (1) Å
$b = 9.835$ (1) Å
$c = 13.263$ (1) Å
$\beta = 114.19$ (1)°
$V = 1492$ Å^3
$Z = 4$
$F(000) = 528$
μ(Cu Kα) = 15.07 cm^{-1}

d(calcd) = 1.140 g cm^{-3}
recording temp: 20 °C
Cu Kα radiation ($\lambda = 1.540\,51$ Å), Ni filtered
θ range: $2° < \theta < 60°$
data collected: 2238
data $I > 3\sigma(I)$: 1639
cryst size: 0.2 × 0.2 × 0.2 mm
$R^a = 0.066$
$R_w{}^b = 0.038$

$^a R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $^b R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table II. Atomic Coordinates with Esd's

atom	10^4X	10^4Y	10^4Z
P	3036 (1)	2979 (1)	8003 (1)
N1	2838 (3)	2969 (4)	6667 (3)
C1	3548 (5)	3933 (5)	6344 (4)
C2	2782 (5)	5055 (5)	5590 (3)
N4	2147 (3)	5860 (4)	6124 (3)
C3	2971 (4)	6725 (4)	7052 (3)
C4	2586 (4)	6809 (5)	8011 (3)
C5	2913 (4)	5567 (5)	8755 (3)
N3	2349 (3)	4298 (4)	8200 (3)
C6	1137 (4)	4023 (5)	8015 (3)
C7	933 (4)	2490 (5)	7764 (4)
N2	2074 (3)	1852 (4)	8039 (3)
C8	2036 (4)	549 (5)	7468 (4)
C9	1789 (5)	768 (5)	6251 (4)
C10	2655 (5)	1666 (5)	6098 (4)
B1	4585 (5)	2698 (6)	8971 (5)
B2	1101 (5)	6749 (6)	5228 (4)

Single crystals of compound **5** could be grown, allowing the first structure determination by X-ray diffraction analysis of an "open" tetracyclic tetraaminophosphorane derivative. Its relevance should extend not only to the series of polycyclic polyaminophosphoranes, which includes cyclen- and cyclamphosphoranes and their open-form BH_3 adducts, but also to some of their transition-metal adducts.

Experimental Section

Compound **5** was prepared from cyclamphosphorane and B_2H_6 in toluene at 0 °C on a vacuum line.[5]

Suitable colorless prismatic crystals of **5** were obtained from a saturated solution of **5** in CH_2Cl_2 by slow evaporation at 0 °C. These crystals are monoclinic and belong to space group $P2_1/c$. The unit cell parameters given in Table I have been refined by least squares from angular positions of 25 reflections.

The intensities of 2238 reflections were collected with an Enraf-Nonius CAD4 automated diffractometer (κ diffraction geometry; *hkl*, –*hkl*). No decrease in the intensity of the standard reflections (30$\bar{4}$, 3$\bar{2}\bar{6}$, 0$\bar{2}$7) recorded periodically was observed during the data collection. The data were corrected for Lorentz and polarization factors, but not for absorption. The structure was solved by direct methods (MULTAN).[6] Fourier synthesis allowed the location of all non-hydrogen atoms. A preliminary refinement by a least-squares method[7] (XFLSN program)[8] was made on 1639 reflections to reach R_w and R values of 0.10. At this stage of refinement, a Fourier difference map showed the hydrogen atoms. They were introduced isotropically but not refined ($B = 6$ Å^2). The final R_w and R factors reached values of 0.038 and 0.066.

Final atomic coordinates are shown in Table II and selected bond lengths and angles in Table III. The molecular structure and the labeling of the atoms are shown in Figure 1.

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Table III. Selected Bond Lengths (Å) and Angles (deg) with Esd's

P-N3	1.637 (4)	N3-C5	1.473 (5)
P-N2	1.653 (4)	N3-C6	1.462 (5)
P-N1	1.686 (3)	N4-C2	1.491 (5)
P-B1	1.858 (5)	N4-C3	1.505 (5)
N4-B2	1.619 (6)	C1-C2	1.534 (6)
N4-H	1.217 (3)	C3-C4	1.535 (5)
		C4-C5	1.518 (5)
N1-C10	1.457 (5)	C6-C7	1.544 (6)
N1-C1	1.479 (5)	C8-C9	1.530 (6)
N2-C7	1.466 (5)	C9-C10	1.477 (6)
N2-C8	1.479 (5)		
N3-P-N2	95.1 (2)	C6-N3-C5	119.6 (4)
N3-P-N1	108.2 (2)	C6-N3-P	113.9 (3)
N2-P-N1	103.3 (2)	C5-N3-P	125.1 (3)
N3-P-B1	118.5 (2)	H-N4-C2	100.0 (3)
N2-P-B1	116.7 (2)	H-N4-C3	111.4 (3)
N1-P-B1	112.8 (2)	H-N4-B2	109.9 (3)
C10-N1-P	118.3 (3)	C2-N4-C3	111.6 (4)
C10-N1-C1	113.5 (4)	C2-N4-B2	111.5 (4)
C1-N1-P	117.0 (3)	C3-N4-B2	111.9 (4)
C7-N2-C8	114.8 (4)		
C7-N2-P	110.8 (3)		
C8-N2-P	116.0 (3)		

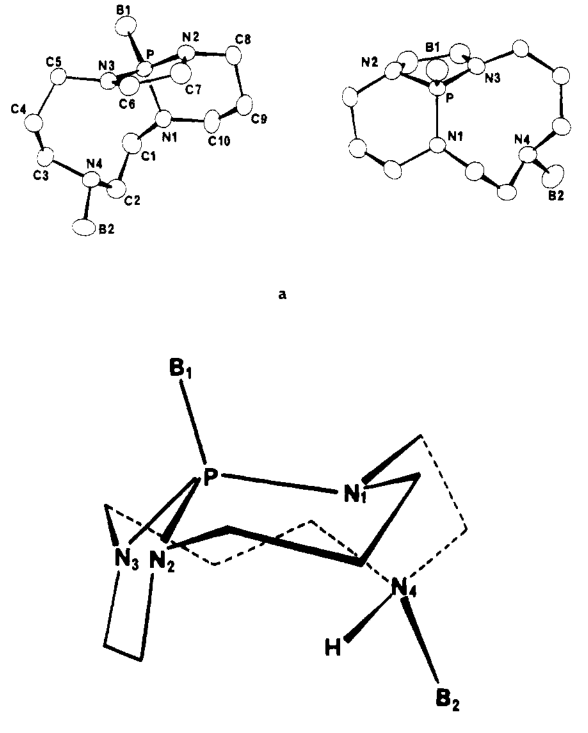

Figure 1. Structure of cyclamphosphane–bis(borane): (a) two ORTEP drawings of **5**; (b) conformation of the molecule.

Table IV. P–B Bond Length in Compounds Containing the λ^4-P–BH_3 Linkage

molecule	P–B length, Å	method[a]	ref
$PF_3{\cdot}BH_3$	1.836 (12)	MW	10
5	1.858 (5)	XR	this work
$H_3B{\cdot}P[OCH_2CH_2]_2N{\cdot}BH_3$	1.873 (7)	XR	11
$(H_2N)_3P{\cdot}BH_3$	1.887 (13)	XR	12
$[(CH_3)_2P{\cdot}BH_3]_2$	1.951 (21)	XR	13
B–P (blende structure)	1.964	XR	14

[a] Abbreviations: MW, microwave; XR, X ray.

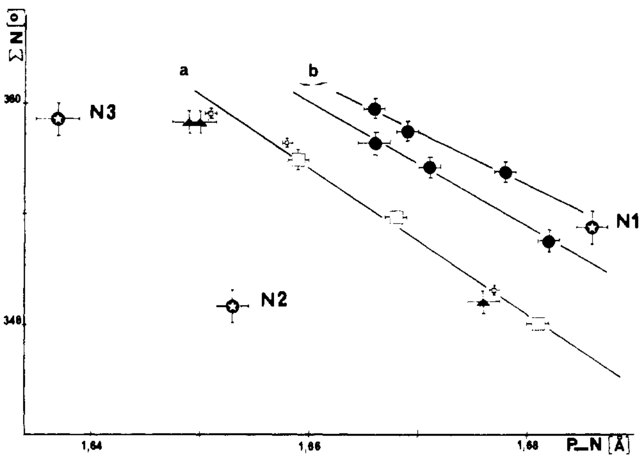

Figure 2. P–N bond length vs. sum of bond angles around nitrogen in five (λ^4-P)(λ^3-N)$_3$-containing compounds: (a) tris(piperidino)phosphane selenide (small squares), tris(morpholino)phosphane selenide (large squares), and tris(dimethylamino)phosphane selenide (triangles);[16] (b) tris(dimethylamino)phosphane (circles) coordinated to the Fe atom in $[(Me_2N)_3P]_2Fe(CO)_3$;[17] (c) bisadduct **5** (circles with stars).

Results and Discussion

Only the open form, which has one borane group on phosphorus and the other on the NH site, is detected when the isolated compound **5** is dissolved in toluene. This is established by the ^{31}P NMR spectrum, which exhibits a single low-field 1:1:1:1 quartet (δ = 115 from 85% H_3PO_4; J_{P-B} = 95 Hz); the $^{11}B\{^1H\}$ spectrum consists of a broad singlet at −14.5 ppm (from $Et_2O{\cdot}BF_3$), a position usually found for N-coordinated BH_3 groups, and a doublet (−43.0 ppm; J_{P-B} = 95 Hz) in the region characteristic of P-coordinated BH_3.[9]

In the solid state, the structure of **5** (Figure 1) displays a P–B bond 1.858 (5) Å long, in the usual range known for P–B bonds (1.84–1.96 Å).[10-14] From a number of X-ray diffraction and microwave studies (Table IV), the P–B bond appears, on the whole, to become shorter when the electronegativities of the substituents of phosphorus increase; this can be interpreted as resulting from the stabilization and "shrinking" of the 3d orbitals of the P atom, rendering σ and/or π interactions between the P and B atoms easier. The rather short P–B bond found in **5** is consistent with this trend.

The nitrogen and boron atoms form around the phosphorus atom a slightly distorted tetrahedral arrangement, the N–P–N angles (95.1 (2), 103.3 (2), 108.3 (2)°) being sharper than the N–P–B angles (112.8 (2), 116.7 (2), 118.5 (2)°).

Figure 1 shows that the second borane group is coordinated to the nitrogen atom of the NH site, which is consistent with the shift toward lower frequencies, from 3300 to 3240 cm^{-1}, observed in the IR spectrum (KBr pellet) upon coordination of the ligand. The N–B bond length in **5** (1.619 (6) Å) lies in the usual range for N–BH_3 bonds (1.56–1.66 Å)[11,15] and is only slightly shorter than that reported for $H_3B{\cdot}P(OCH_2CH_2)_2N{\cdot}BH_3$ (1.655 (8) Å).[11] The latter compound is remarkable, since it shows that the nitrogen atom can exhibit strong basicity in spite of its being bound to a phosphorus atom, which usually sharply reduces its basicity toward

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soft Lewis acids such as BH_3.

The P–N bonds, in **5**, present many interesting features: in contrast to the observations of Songstad et al.[16] and Cowley et al.,[17] there is no linear correlation between the three sums ($\sum N$) of the bond angles around the nitrogen atoms and the three corresponding P–N bond lengths. Figure 2 compares our data with those found by these authors for three triaminophosphane selenides and for $[P(NMe_2)_3]_2Fe(CO)_3$. Like **5**, these four compounds possess three tricoordinated nitrogen atoms bound to a tetracoordinated phosphorus atom. All four display two short P–N bonds (1.65–1.67 Å), with the arrangement of the bonds around the nitrogen being essentially coplanar, and one longer P–N bond (1.68 Å), with the nitrogen atom correlatively adopting a more pyramidal configuration (it should however be noted that this value is still lower than that usually expected for P–N "single" bonds, 1.77 Å[11,20]). In contrast, in **5** it is a short P–N bond (P–N2 = 1.653 (4) Å) that corresponds to the nitrogen having the most pyramidal configuration ($\sum N2 = 341.6 \pm 3.0°$). This is likely to be a consequence of the location of N2 at a bridgehead position between the 5- and 6-membered rings.

This means, as in $Cp(CO)PhFe\overline{P(OCH_2CH_2)_2N}$,[18] where a P–N bond of 1.692 Å has been found, with $\sum N = 333.5°$, that the mechanism responsible for the P–N bond shortening is still effective, in spite of the nonplanar geometry of the N atom. The other two P–N bonds fit better into the correlations of Figure 2: a very short P–N3 bond (1.637 (4) Å) with a planar geometry about N3 ($\sum N = 358.6 \pm 3.0°$) and a long P–N1 bond (1.686 (3) Å) with a more pyramidal nitrogen atom ($\sum N = 348.8 \pm 3.0°$). If one adopts the customarily employed model of Pd_π–N p_π interaction,[19] these data suggest strong p_π–d_π interactions between both N2 and N3 and phosphorus and weaker interactions between N1 and P. Such interactions are of course not the only possible origin of the observed bond shortening; the changing from sp^3 to sp^2 hybridization is also expected to contribute to this shortening.[20] It should be noticed that N1 has its lone pair approximately trans (dihedral angle of ca. 180°) to the P–B bond and exhibits a smaller sum of bond angles, in accordance both with Songstad's observations and with Cowley's MO calculations for H_2NPH_2[21] and $P(NH_2)_3$,[22] which show that the nitrogen's geometry moves from trigonal planar toward tetrahedral as the dihedral angle increases from 90 to 180°. These considerations encourage us to investigate the basicity of N1 and N2 in **5** toward Lewis acids such as, for example, BF_3.

Figure 1 shows that the diastereoisomer formed is **5′**, the one in which the P–B and N–B bonds are oriented trans to each other with respect to the mean plane of the molecule. In this conformation, the hydrogen atom of the N4–H bond is located in a cavity in the neighborhood of the N1 (2.3 Å) nitrogen atom. The sharp N4HN1 angle (110°) probably hinders[23,24] the formation of a strong hydrogen bond between H(N4) and N1 atoms, and the interaction between the H(N4) and N2 atoms is also impeded by the fact that the free electron pair of N2 is oriented in the opposite direction with respect to the molecule's mean plane.

The six-membered ring adopts the usual low-energy chair conformation and the five-membered ring a slightly flattened "envelope" conformation whose tip is occupied by the phosphorus atom, which can be taken as indicating the absence of particular constraints in the polycyclic structure.

The results presented in this paper are expected to be relevant to most open tautomeric forms of the tetracyclic tetraaminophosphoranes, such as **1a**, **2**, and their homologues and derivatives, whether they are uncomplexed or act as mono- or bidentate ligands toward Lewis acids; different conformations will, however, have to be adopted in the case of chelation.

Registry No. **5′**, 84237-92-3.

Supplementary Material Available: Tables of F_o and F_c values, B_{ij} values, hydrogen atom coordinates, and nonessential angles (12 pages). Ordering information is given on any current masthead page.

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Raman Spectra of $Co(NH_3)_6X_3$ (X = Cl, Br, I) Complexes

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The vibrational Raman spectra of the complexes $Co(NH_3)_6X_3$ (X = Cl, Br, I) have been measured between 310 and 40 K. The controversial fine structure near 500 cm^{-1} is explained on the basis of inequivalent sites and different isotope shifts for the A_{1g} and T_{1u}^b stretching vibrations. The polarized intensities for the E_g vibration of $Co(NH_3)_6Cl_3$ can be analyzed quantitatively in terms of four inequivalent species. The structure of the iodide complex changes from the high-temperature cubic to a polydomained monoclinic phase near 280 K. Additional structural changes are observed near 250 and 90 K. Off-center displacement in the charge-transfer states of the CoN_6 chromophore may be responsible for the Raman activity of the T_{1u}^b vibration.

1. Introduction

The assignment of the stretching vibrations in $Co(NH_3)_6X_3$ (X = Cl, Br, I) has been a controversial subject for many years.[1-5] Of the two IR-active T_{1u} skeletal modes, the bending vibration is strong in the IR spectrum but the predominantly stretching vibration (T_{1u}^b) is very weak. The IR bands near

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