Table II. Observed and Calculated Electronic Spectral Data for [Co(N_4)(acac)]X Complexes

	abs bands								
	solution[a]			solid state[b]					
compd	λ, nm	ϵ^c	ν, cm^{-1}	λ, nm	ν, cm^{-1}	B′, cm^{-1}	Dq, cm^{-1}	calcd ν, cm^{-1}	assgnts
[Co(3,3,3-N_4)(acac)]PF_6	1009	8	9910	985	10150			10039	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$
	491	34	20370	476	21010	780	1092	20280	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$
								20959	$^4A_{2g} \leftarrow {}^4T_{1g}(F)$
	292	10800	34250						
[Co(3,2,3-N_4)(acac)]PF_6	960	9	10420	979	10220			10543	as above
	476	51	21010	458	21830	820	1149	21320	
								22033	
	292	11000	34250						
[Co(2,3,2-N_4)(acac)]PF_6	995	9	10100	982	10180			10232	as above
	485	50	20620	458	21830	795	1113	20670	
								21362	
	289	7000	34600						
[Co(3,3,3-N_4)(acac)]I	1020	8	9800	1026	9750			10374	as above
	491	31	20370	488	20490	772	1080	20072	
								21174	
	293	9100	34130						
[Co(3,2,3-N_4)(acac)]I	999	8	10010	983	10170			10144	as above
	486	37	20580	468	21370	788	1103	20488	
								21174	
	292	10300	34250						
[Co(2,3,2-N_4)(acac)]I	990	6	10100	990	10100			10232	as above
	482	40	20750	485	20620	795	1113	20670	
								21362	
	292	11200	34250						

[a] Solution spectra were obtained by using concentrations of ~1 × 10^{-1} M (tetrachloroethylene, C_2Cl_4), ~1.0 × 10^{-2} M (methanol), and ~1.0 × 10^{-3} M (methanol), one for each band going from low energy to high energy. [b] Solid-state spectra were obtained by using the Nujol mull diffuse-transmittance technique.[23] [c] Molar absorptivities, L mol^{-1} cm^{-1}.

Both visual and numerical comparison of the diffraction lines show that the patterns are identical and that the compounds are isomorphic.

Conclusions

While there is no doubt that the 12 complexes prepared in this study have pseudooctahedral structures, visible spectra cannot be used to determine whether the compounds exist in the α-cis or β-cis isomeric forms or a mixture thereof. Proton magnetic resonance studies are precluded by the paramagnetic nature of both metal ions. This leaves infrared spectral data as the only source for conjecture.

In the infrared spectra of [M(2,3,2-N_4)(acac)]PF_6 and [M(3,2,3-N_4)(acac)]PF_6, the presence of only one isomer is suggested by the uncomplicated nature of the nitrogen–hydrogen stretching vibrations observed. A mixture of isomers may be indicated by the more complicated patterns of the corresponding iodide salts; however, in these compounds, selective hydrogen bonding of one set of amine protons to the iodide ion causes a shift of some of these stretching vibrations to lower energies. Infrared spectra of the [M(3,3,3-N_4)(acac)]PF_6 and [M(3,3,3-N_4)(acac)]I complexes show the most complicated stretching patterns for the amine protons and are most likely to exist as a mixture of isomers because of greater flexibility associated with longer carbon chains. Indeed, isomer studies of tetraamine complexes[32] have shown that as the chain length increases, the trans form is favored and only the β-cis form exists in the presence of a bidentate ligand. It is likely that the β-cis form dominates in the (3,2,3) and (3,3,3) complexes prepared in this study, but the differences in numbers of IR bands may be due to solid-state effects only.

Attempts to prepare macrocyclic tetraaza complexes via the acid-catalyzed (pH ~ 3) rearrangement of the [Ni(N_4)(acac)]X complexes in aqueous solution were unsuccessful. Three hours of refluxing followed by addition of 1 equiv of KX always resulted in the formation of the corresponding tetraamine, [Ni(N_4)X_2], which was identified on the basis of its infrared spectrum. Under the same conditions, nickel complexes containing similar sexadentate Schiff base ligands do react to form the desired macrocycles.[7,8] This suggests that 2 equiv of β-diketone are necessary for ring closure to occur. This hypothesis was tested by refluxing acidic solutions of the [Ni(N_4)(acac)]X complexes in the presence of an additional 1 equiv of 2,4-pentanedione. Small amounts of the macrocyclic species are produced;[33] however, the mechanism involved here cannot be distinguished from the in situ procedure previously reported.[7,8] The latter procedure continues to provide the best means of synthesis of macrocyclic complexes with uninegative Schiff base ligands.

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Supplementary Material Available: Tables of analytical data along with yields and colors of individual complexes and magnetic susceptibility data (1 page). Ordering information is given on any current masthead page.

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A Theoretical Study of the HP_4 Ion

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Baudler et al.[1] recently reported the reduction of tetraphosphorus (**1**) to an anion (**2** or **3**) which can be regarded as the monoconjugate base from tetraphosphabicyclobutane (**4**). The NMR spectrum of the ion in solution showed three different

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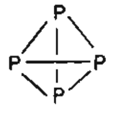
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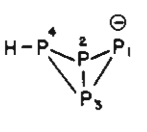

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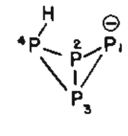

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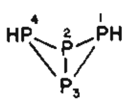

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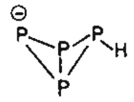

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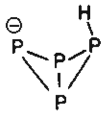

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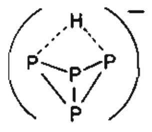

7

phosphorus resonances, implying that degenerate rearrangement by migration of hydrogen from P4 to P1 (i.e. **2** → **5** or **3** → **6**) is slow on the NMR time scale. This suggests that the ion has the anti structure (**2**) because interconversion of the syn isomers (**3** and **6**) would be expected to take place very rapidly, given that it involves only a small displacement of hydrogen and given that it could take place by tunneling. Furthermore, other analogous phosphorus compounds have been shown[2] to have anti geometries.

Since AM1[3] parameters are now available[4] for phosphorus, we have used them to study **1–4**. The calculations were carried out by using the standard AM1 procedure as implemented in the AMPAC2.1 program.[5] The calculated geometries and heats of formation are shown in Table I, and the calculated formal charges, in Table II.

AM1 seemingly overestimates strain energies due to P–P–P bending, the heat of formation calculated for **1** being too positive by 36.3 kcal/mol.[3] The heats of formation calculated for **1–8** are therefore probably all too large, by a lesser amount. However, since the strain energies of all these species should in any case be similar, the errors should not affect their relative energies, which are the quantities of interest here.

The syn isomer **3** is predicted to be not only lower in energy than **2** but much lower, the difference between their calculated heats of formation being 11.5 kcal/mol. While the AM1 parameters for phosphorus have not been tested as thoroughly as those for the "organic" elements, these results seem to suggest strongly that **3** is indeed the more stable isomer. This would eliminate the most natural explanation for the relative slowness of the interconversion of **3** and **6**. We also examined the alternative possibility, that interconversion of **3** and **6** might be slow on the NMR time scale. However, the calculated barrier was, as expected, very low (2.2 kcal/mol). The properties of the corresponding transition state (**7**), which had C_{2v} symmetry, are shown in Tables I and II. The results in Table I also indicate that **4** is a strong acid, its calculated deprotonation energy being only 306 kcal/mol. AM1 has been shown[6] to give good estimates of proton affinities and deprotonation energies.

The experimental studies were carried out for the sodium salt of **2** (**3**) in solution whereas our calculations refer to the isolated anions. The apparent discrepancy between them might then be due to ion pairing. Ion pairing might either selectively stabilize the anti isomer (**2**) or inhibit the rearrangement of **3**.

Table I. Calculated Properties of P_4 Compounds

		bond lengths, Å		
compd	$\Delta H_f{}^a$	P1–P2	P2–P3	P2–P4
1	50.4	2.040	2.040	2.040
2	−13.4	2.019	1.974	2.105
3	−25.0	1.960	2.037	2.022
4	36.2	2.014	2.048	2.014
7	−22.8	2.009	2.015	2.007

[a] Heat of formation (kcal/mol).

Table II. Calculated Formal Atomic Charges

	formal atomic charges[a] at			
compd	P1	P2	P4	H
2	−0.6430	−0.0130	−0.4010	0.0701
3	−0.8670	−0.0995	−0.5212	0.1898
4	0.1220	−0.1751	0.1219	0.0531
7	−0.7727	0.1098	−0.7804	0.3332

[a] In units of the electronic charge.

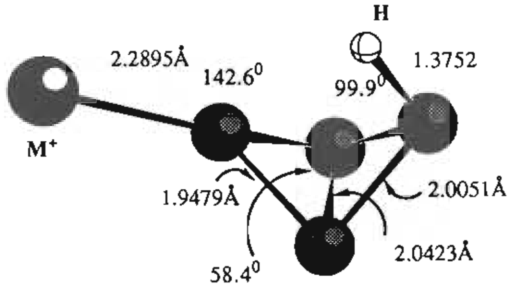

Figure 1. Geometry calculated for the adduct between a sparkle (M^+) and **2**.

Since AM1 parameters are not yet available for sodium or potassium, we checked these possibilities by using a disembodied unit positive charge ("sparkle")[5] as a model for the metal cation, placing it near the negatively charged phosphorus atom in **2** or **3**. The resulting "ion pair" (**8**) still had syn hydrogen, its structure being shown in Figure 1. However, conversion of **8** to the corresponding species derived from **6**, without moving the sparkle, was stongly endothermic (ΔH + 13 kcal/mol) and no path of lower energy was found for the hydrogen migration.

Our results thus support the second suggestion above, i.e. that **3** rearranges slowly in solution because of inhibition by ion pairing.

The situation is reminiscent of that involved in the reduction of ketones by sodium borohydride in aprotic solvents, where association of Na^+ with the carbonyl oxygen facilitates reaction:[7,8]

$$\mathrm{H_3BH^-\ C{=}O{\cdots}Na^+ \rightarrow H_3B\ H{-}C{-}O^-Na^+} \qquad (1)$$

If the sodium ions are prevented from associating with carbonyl by adding crown-6 ether, the reaction is completely inhibited.[8] If the rearrangement of **3** is indeed inhibited by ion pairing, it should then take place rapidly in the presence of a crown ether able to sequestrate the metal ion.

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Registry No. HP_4^-, 134682-45-4.

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