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Characterization of the P^+L_n Ion Molecule Clusters of the First- and Second-Row Hydrides

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Abstract: G1 and G2 methodologies have been used to characterize P^+L_n ($n = 1$, 2 and L = NH_3, OH_2, FH, PH_3, SH_2, ClH) ion–molecule complexes in both singlet and triplet states. A topological analysis of their electron density and its associated Laplacian has been carried out in order to characterize the nature of the ion–ligand bond. Both triplet and singlet P^+ behave as a soft acid, for which electronic effects are dominant in the bonding. In general, the results are in close agreement with the hard–soft acid–base principle (HSAB). Thus, P^+ prefers to be bonded to the softest bases. For two-ligand complexes, lower binding energies and greater energy differences between triplet and singlet states are observed. For the singlets, although there exists a decrease in the covalency of the bond, electronic effects still have considerable importance, whereas for the triplets, a greater dominance of electrostatics in the bonding is predicted along with a concomitant larger lowering of binding energies.

1. Introduction

The study of ion–molecule clusters is a research field of increasing interest.[1] This is motivated because clusters constitute a bridge between the gas and condensed phases and the study of the formation of cluster ions is relevant to the understanding of phenomena such as nucleation, the development of surfaces, catalysis, solvation, acid–base chemistry, combustion, and atmospheric processes. Determination of the binding energies (D_e) as the cluster grows up along with geometric characterization has been the subject of several theoretical end experimental studies.[2] The nature of the bond between the ion and the neutral ligand molecule focuses special attention. Both electrostatic and electronic interactions have been claimed to take part in the binding mechanism of M^+L_n complexes. The relative importance of each interaction depends upon the nature of the ion, the nature of the ligand, and the number of them bonded to the ion. For closed shell ions, the bond is predominantly due to electrostatics, whereas for open shell ions, electronic effects are also present and usually stronger ion–ligand bonds are encountered. Depending on the ligand, the electronic effects are more or less pronounced. The number of ligands attached to the ion is also important. Thus, it has been observed that, as the number of ligands increases, lower D_e's are obtained. This lowering is more pronounced for open shell ions than for closed shell ones. Also, it has been found that when the cluster grows up to two or three ligands the D_e's are similar through different ions.[2] This behavior suggests that, as the number of ligands increases, for open shell ions the electronic effects lose their importance and the bond becomes predominantly electrostatic.

In two recent papers,[3,4] we reported an ab-initio study of triplet $P(NH_3)_n^+$, $P(OH_2)_n^+$ ($n = 1$, 2), and $P(NH_3)(OH_2)^+$ ion–molecule complexes, along with a topological analysis of their electron density ($\varrho(\mathbf{r})$), its associated Laplacian ($-\nabla^2\varrho(\mathbf{r})$), and the properties of the bond critical points. One-ligand complexes presented a much larger D_e than two-ligand ones, even larger than one should expect from electrostatic considerations. Inspection of the topological features of the Laplacian, along with analysis of the properties of the bond critical points, pointed out the presence of significant electron donation for one-ligand complexes, responsible for the enhanced D_e. This electronic interaction was also present in the two-ligand complexes, however to a lesser extent. Correspondingly, the D_e's obtained for them were much lower and closer to typical D_e's values of closed shell ions. The effect of the ligand was also analyzed. For one-ligand complexes, the D_e of NH_3 was found to be larger than for OH_2. The study of the properties of the charge density function revealed that this behavior had its origin in the greater electron donation ability of ammonia. These electronic effects were diminished in the two-ligand complexes, hence their D_e's become similar.

In this paper, we have carried out a G1 and a G2 study of the P^+L_n ($n = 1$, 2) systems for L = NH_3, OH_2, FH, PH_3, SH_2, and ClH, for both their singlet and triplet states. Binding energies and atomic charges have been also calculated. In order to characterize the ion–molecule interaction, we have performed a topological analysis of the electron density $\varrho(\mathbf{r})$ and its associated Laplacian $\nabla^2\varrho(\mathbf{r})$. Bond critical point properties were also analyzed. It is the aim of this study to extend the previous studies to ligands that comprise second row atoms and to different spin states of the phosphorus. The difference in bonding between the ligands and the different behaviors of the singlet and triplet states of P^+ are also discussed.

2. Methods

All structures were optimized at the MP2/6-31G(d) level of theory.[5] Geometries of these species can be found in Figures 1, 2, 3, and 4. Analytical frequencies at the stationary points were calculated at the MP2/6-31G(d) level of theory, and all of them were found to be positive.

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Table 1. MP4/6−311G(d,p), G1, and G2 Energies and the Corrections to the Base Level Energy for the One-Ligand Complexes[a]

species		MP4/6−311G(d,p)	ΔE^{+}	ΔE^{2df}	ΔE^{QCI}	ΔE^{ZPE}	E_{G1}	Δ	E_{G2}
$P(NH_3)^+$	$^3A_2$	−396.976 434	−3.759	−51.327	−2.329	40.085	−397.024 844	−8.377	−397.027 521
	$^1A'$	−396.917 843	−3.638	−57.657	−9.025	38.732	−396.986 271	−8.922	−396.988 353
$P(OH_2)^+$	$^3A''$	−416.780 652	−6.397	−60.490	−1.712	24.543	−416.855 788	−7.640	−416.857 728
	$^1A_1$	−416.738 272	−6.000	−67.260	−4.054	24.661	−416.827 765	−7.679	−416.828 604
$P(FH)^+$	$^3A''$	−440.729 810	−7.887	−68.564	−1.067	10.864	−440.827 544	−7.995	−440.829 839
	$^1A'$	−440.671 121	−7.712	−76.474	−7.636	11.008	−440.788 775	−8.329	−440.790 264
$P(PH_3)^+$	$^3A_2$	−683.175 539	−3.762	−60.343	−3.558	30.634	−683.245 326	−6.446	−683.246 072
	$^1A'$	−683.122 004	−3.696	−68.127	−7.395	28.687	−683.209 375	−7.097	−683.209 632
$P(SH_2)^+$	$^3A''$	−739.377 591	−4.209	−73.556	−3.364	19.423	−739.470 377	−5.805	−739.470 482
	$^1A_1$	−739.333 954	−3.727	−85.215	−4.099	18.767	−739.445 068	−8.194	−739.446 422
$P(ClH)^+$	$^3A''$	−800.725 126	−5.651	−84.231	−2.697	8.822	−800.839 963	−5.001	−800.839 264
	$^1A'$	−800.675 824	−5.802	−94.839	−6.149	9.087	−800.810 368	−5.839	−800.809 367

[a] Base, G1, and G2 energies are given in hartrees and corrections to the base level energy in millihartrees.

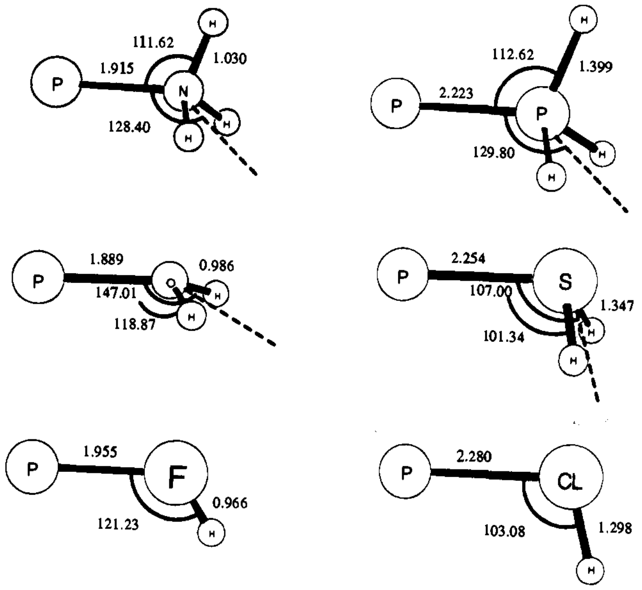

Figure 1. MP2/6-31G(d) geometries of the triplet one-ligand ion–molecule complexes. Distances are in Å and angles in degrees.

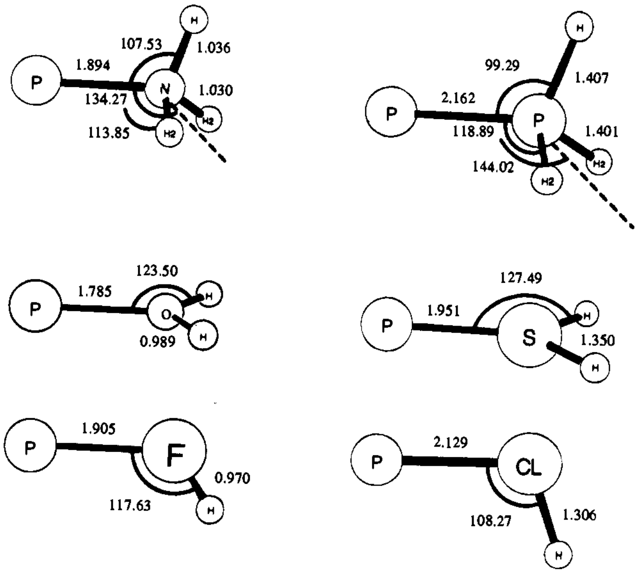

Figure 2. MP2/6-31G(d) geometries of the singlet one-ligand ion–molecule complexes. Distances are in Å and angles in degrees.

G1 and G2 methodologies[6–8] have been used to evaluate the energies. In the G1 theory, several corrections are made to the MP4/6-311G-(d,p)//MP2/6-31G(d) base level energy to correct for the deficiencies in the basis set and in the method. The incompleteness of the basis set is corrected through the consideration of diffuse functions (ΔE^{+}), and extra d- and f-functions for non-hydrogen atoms (ΔE^{2df}). The deficiencies in the method are partially overcome by QCISD(T) calculations (ΔE^{qci}) and an empirical high-level correlation (ΔE^{HLC}). Since qualitative differences between HF and MP2 geometries have been found for some complexes, we have evaluated the zero-point vibrational energy (ZPVE) correction at the MP2/6-31G(d) level of theory, instead of the proposed HF one. Taking into account the above contributions, the E_{G_1} is the result of several additive corrections to the base level energy, namely

$$E_{G_1} = MP4/6 - 311G(d,p) + \Delta E^{+} + \Delta E^{2df} + \Delta E^{qci} + \Delta E^{HLC} + (ZPVE)_{MP2/6-31G(d)} \quad (1)$$

It has been observed that G1 theory does poorly on D_e for some ionic molecules, for some triplet singlet gaps, and for some hydrides.[6,7] Since it has been reported that G2 seems to overcome these difficulties,[8] we have also applied the G2 methodology to our systems. The G2 level adjusts the G1 energy, including corrections for the larger 6-311+G-(3df,2p) basis set, the additive assumption of the G1 corrections, and providing an empirical correction to HLC for the number of valence electron pairs. Thus

$$G2 = G1 + \Delta + n_{pair}\text{correction} \quad (2)$$

$$\Delta = MP2/6 - 311 + G(3df,2p) - MP2/6 - 311G(2df,p) - MP2/6 - 311 + G(d,p) + MP2/6 - 311G(d,p) \quad (3)$$

All G1 and G2 calculations have been performed using the GAUSSIAN 92 code of programs.[9]

G1 and G2 energies with their corresponding corrections to the E_{Base} can be found in Tables 1 and 2. The energy gaps between triplet and singlet states for the 12 ion–molecule complexes are depicted in Table 3. Using these energies, we have evaluated the D_e's as the energy difference between the ion–molecule complexes and their original reactives in their appropriate spin state, thus

$$(D_e)_{PL_n} = E_{PL_n} - (E_{PL_{n-1}} + E_L) \quad (4)$$

The values of the binding energies for one- and two-ligand complexes have been collected in Tables 4 and 5, respectively. The influence of the basis set superposition error (BSSE) on the binding energies has been estimated with the counterpoise method.[10,11] It has been found

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Table 2. MP4/6−311G(d,p), G1, and G2 Energies and the Corrections to the Base Level Energy for the Two-Ligand Complexes[a]

species		MP4/6−311G(d,p)	ΔE^{+}	ΔE^{2df}	ΔE^{QCI}	ΔE^{ZPE}	E_{G1}	Δ	E_{G2}
$P(NH_3)_2^+$	$^3A_{2g}$	−453.441 816	−5.385	−81.148	−1.399	77.796	−453.507 592	−16.069	−453.513 401
	$^1A_1$	−453.450 756	−4.969	−90.379	−1.694	82.004	−453.527 194	−16.759	−453.532 553
$P(OH_2)_2^+$	^3A	−493.095 546	−12.786	−99.300	−0.232	48.438	−493.215 066	−15.168	−493.219 974
	$^1A_1$	−493.084 925	−11.058	−109.118	−0.659	51.809	−493.215 351	−14.410	−493.218 361
$P(FH)_2^+$	^3B_g	−541.047 930	−15.842	−117.407	+0.353	21.806	−541.198 818	−14.979	−541.203 537
	^1A	−540.985 238	−14.720	−128.308	−0.684	24.161	−541.166 189	−14.215	−541.169 004
$P(PH_3)_2^+$	$^3A''$	−1025.825 529	−5.507	−92.458	−5.013	54.886	−1025.929 261	−13.652	−1025.932 653
	$^1A_1$	−1025.872 660	−6.012	−114.096	−3.735	59.924	−1025.997 978	−12.760	−1025.999 338
$P(SH_2)_2^+$	^3B_g	−1138.263 827	−7.229	−121.717	−3.648	36.596	−1138.415 465	−11.988	−1138.417 193
	$^1A_1$	−1138.274 346	−7.048	−141.381	−3.774	40.960	−1138.446 988	−11.674	−1138.447 262
$P(ClH)_2^+$	^3A	−1261.000 001	−8.923	−144.696	−2.599	16.877	−1261.194 982	−10.818	−1261.195 540
	^1A	−1260.975 568	−9.363	−160.923	−3.162	19.732	−1261.190 684	−9.760	−1261.189 044

[a] Base, G1, and G2 energies are given in hartrees, and corrections to the base level energy in millihartrees.

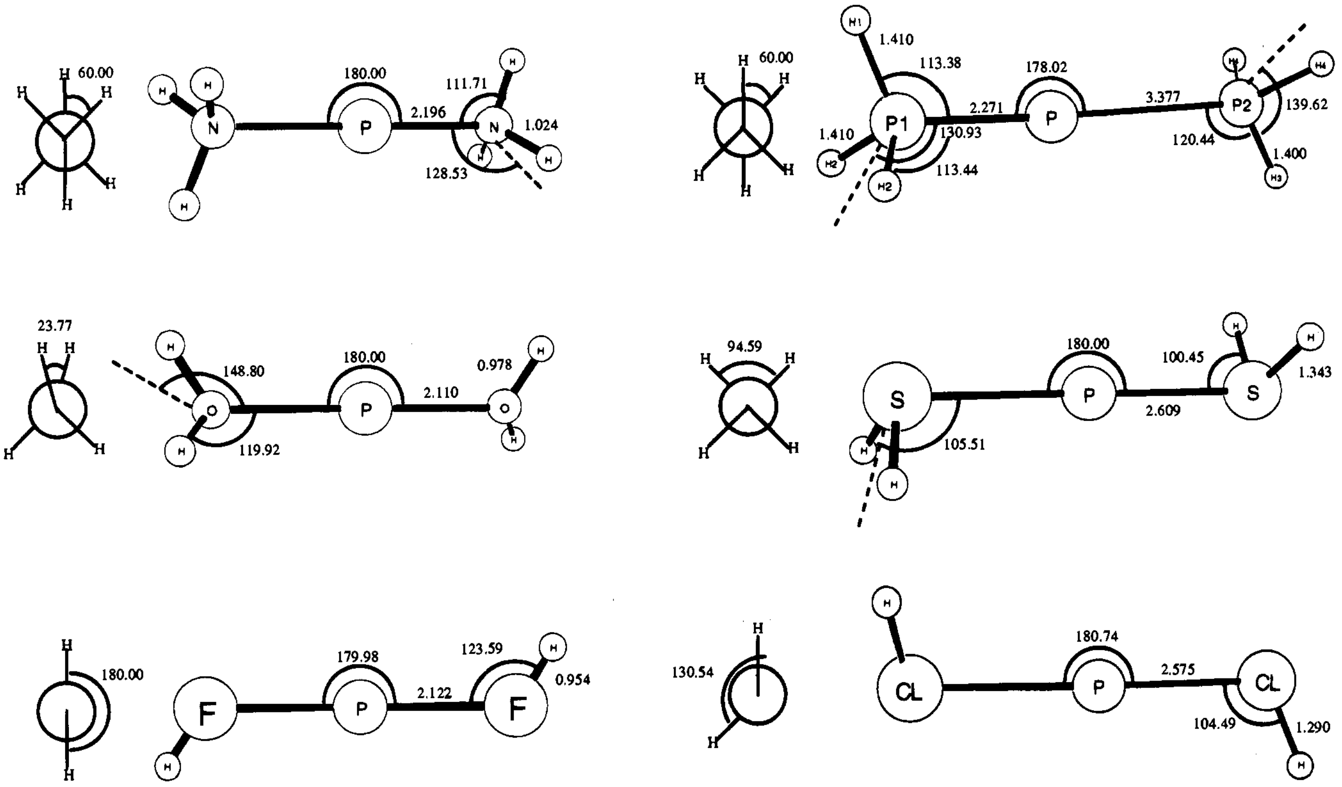

Figure 3. MP2/6-31G(d) geometries for the triplet two-ligand ion−molecule complexes. Distances are in Å and angles in degrees.

Table 3. Energy Gap (kcal/mol) between the Triplet and Singlet States at Different Levels of Theory

species	Δ_{t-s}^{Base}	Δ_{t-s}^{G1}	Δ_{t-s}^{G2}
P^+	−40.75	−24.63	−25.20
$P(NH_3)^+$	−36.77	−24.22	−24.58
$P(NH_3)_2^+$	5.59	12.28	12.03
$P(OH_2)^+$	−26.59	−17.59	−18.27
$P(OH_2)_2^+$	−6.66	0.19	−1.03
$P(FH)^+$	−36.84	−24.31	−24.81
$P(FH)_2^+$	−39.34	−20.47	−21.66
$P(PH_3)^+$	−33.59	−22.56	−22.88
$P(PH_3)_2^+$	29.63	43.12	41.81
$P(SH_2)^+$	−27.41	−15.91	−15.09
$P(SH_2)_2^+$	6.56	19.81	18.87
$P(ClH)^+$	−30.94	−18.59	−18.78
$P(ClH)_2^+$	−15.38	−2.69	−4.06

that even for the worst cases the estimation is not larger than 1.0 kcal/mol, namely BSSE is 0.5 kcal/mol for triplet $(PNH_3)^+$ at the HF/6-311+G(3df,2p) level of theory. This demonstrates that the effect of the BSSE on the dissociation energies is negligible; hence, we shall not include corrections for BSSE hereafter.

We have explored the bonding characteristics of these complexes by means of the Bader's topological analysis of $\varrho(\mathbf{r})$ and $-\nabla^2\varrho(\mathbf{r})$,[12] using the AIMPAC series of programs.[13] We have employed the MP2/MC-311G(d,p)//MP2/6-31G(d) wave functions to build up the electron density. Plots of the Laplacians are depicted in Figures 5 and 6, for all complexes. Properties of the bond critical point (r_c), such as $\varrho(r_c)$, $\nabla^2\varrho(r_c)$, and the value of the energy density $H(r_c)$, are found in Tables 6 and 7. The energy density at the bond critical point indicates a bond to be covalent if $H_{r_c} < 0$ and ionic if $H_{r_c} > 0$.[14] This criterion will serve us to discuss the degree of electronic stabilization in the binding mechanism.

Atomic charges have been evaluated too. For one-ligand complexes, three methods were used, Mulliken, natural, and Bader, while for the two-ligand complexes, only Mulliken and natural were employed. Mulliken charges were calculated using GAUSSIAN 92,[9] and natural and Bader charges, using NBO[15] and AIMPAC program packages.[13]

Hardness (η) of triplet and singlet P^+ has been calculated at the G2 level of theory, using the formula

$$\eta = (I - A)/2 \qquad (5)$$

where I and A are the ionization potential and the electron affinity,

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Table 4. D_e at MP4/6−311G(d,p), G1, and G2 levels of Theory and the Corrections to the Base D_e for the One-Ligand Complexes[a]

species		D_e^{Base}	D_e^{+}	D_e^{2df}	D_e^{QCI}	D_e^{ZPE}	D_e^{G1}	D_e^{Δ}	D_e^{G2}
$P(NH_3)^+$	$^3A_2$	−86.61	3.03	−5.82	−0.20	3.01	−86.57	0.76	−85.80
	$^1A'$	−90.59	3.20	−5.37	3.62	2.16	−86.98	0.55	−86.43
$P(OH_2)^+$	$^3A''$	−59.11	4.23	−6.01	−0.05	1.92	−59.03	1.12	−57.90
	$^1A_1$	−73.27	4.56	−5.84	6.50	2.00	−66.06	1.22	−64.84
$P(FH)^+$	$^3A''$	−28.68	4.08	−5.74	0.17	1.05	−29.11	0.37	−28.73
	$^1A'$	−32.59	4.28	−6.29	4.07	1.14	−29.42	0.29	−29.13
$P(PH_3)^+$	$^3A_2$	−77.70	−0.42	−9.64	−0.08	3.48	−85.44	1.11	−84.33
	$^1A'$	−84.86	−0.29	−10.10	5.53	2.26	−87.50	0.83	−86.66
$P(SH_2)^+$	$^3A''$	−60.47	−0.47	−9.56	−0.37	2.33	−68.55	1.77	−66.78
	$^1A_1$	−73.81	−0.08	−12.45	7.19	1.92	−77.27	0.40	−76.89
$P(ClH)^+$	$^3A''$	−32.61	−1.60	−9.41	−0.31	1.18	−42.75	1.82	−40.91
	$^1A'$	−42.42	−1.60	−11.64	5.54	1.34	−48.78	1.43	−47.33

[a] All values are in kcal/mol.

Table 5. D_e at MP4/6−311G(d,p), G1, and G2 levels of Theory and the Corrections to the Base D_e for the Two-Ligand Complexes[a]

species		D_e^{Base}	D_e^{+}	D_e^{2df}	D_e^{QCI}	D_e^{ZPE}	D_e^{G1}	D_e^{Δ}	D_e^{G2}
$P(NH_3)_2^+$	$^3A_{2g}$	−23.43	2.93	−0.81	0.82	1.53	−18.98	0.48	−18.49
	$^1A_1$	−65.79	3.11	−2.63	4.84	5.02	−55.48	0.38	−55.10
$P(OH_2)_2^+$	^3A	−24.34	2.79	−0.89	0.92	1.52	−20.00	0.46	−19.56
	$^1A_1$	−44.28	3.63	−2.80	2.13	3.55	−37.78	0.97	−36.79
$P(FH)_2^+$	^3B_g	−17.91	2.60	−1.86	0.71	1.09	−15.36	0.29	−15.08
	^1A	−25.36	3.19	−3.73	4.18	2.48	−19.20	0.98	−18.23
$P(PH_3)_2^+$	$^3A''$	−5.44	−0.60	−0.41	0.21	−0.52	−5.72	−0.10	−5.80
	$^1A_1$	−68.66	−0.95	−9.11	3.43	3.86	−71.41	0.87	−70.48
$P(SH_2)_2^+$	^3B_g	−9.64	−1.17	−2.11	0.54	0.91	−11.45	0.81	−10.69
	$^1A_1$	−43.61	−1.35	−7.14	0.92	4.06	−47.17	2.50	−44.66
$P(ClH)_2^+$	^3A	−7.59	−1.54	−2.98	0.42	0.69	−10.97	0.59	−10.38
	^1A	−23.16	−1.73	−6.51	2.24	2.32	−26.88	1.78	−25.09

[a] All values are in kcal/mol.

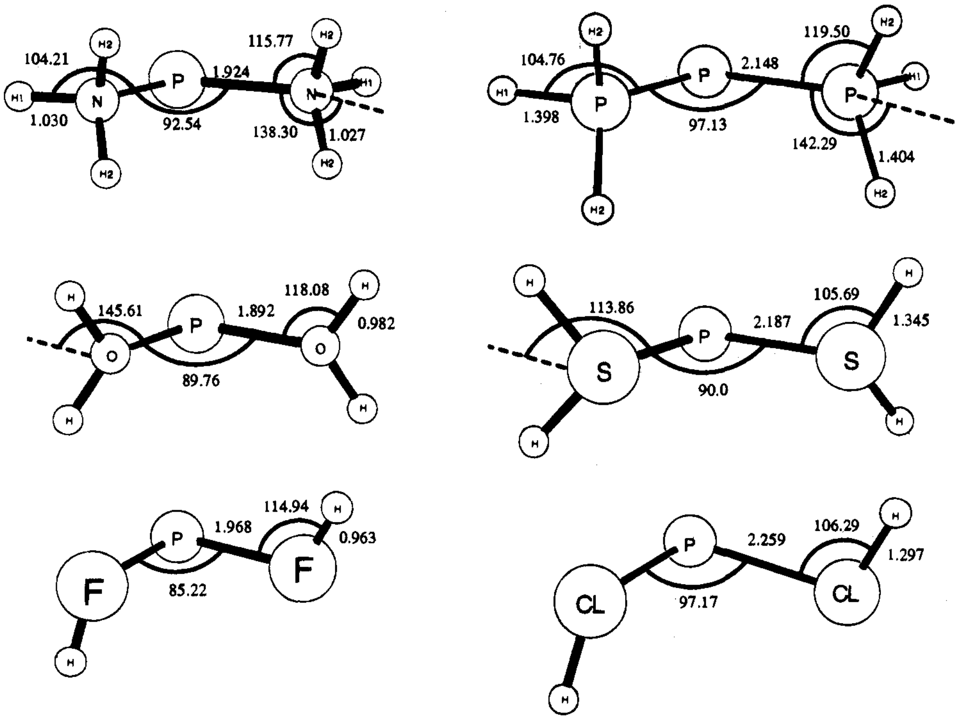
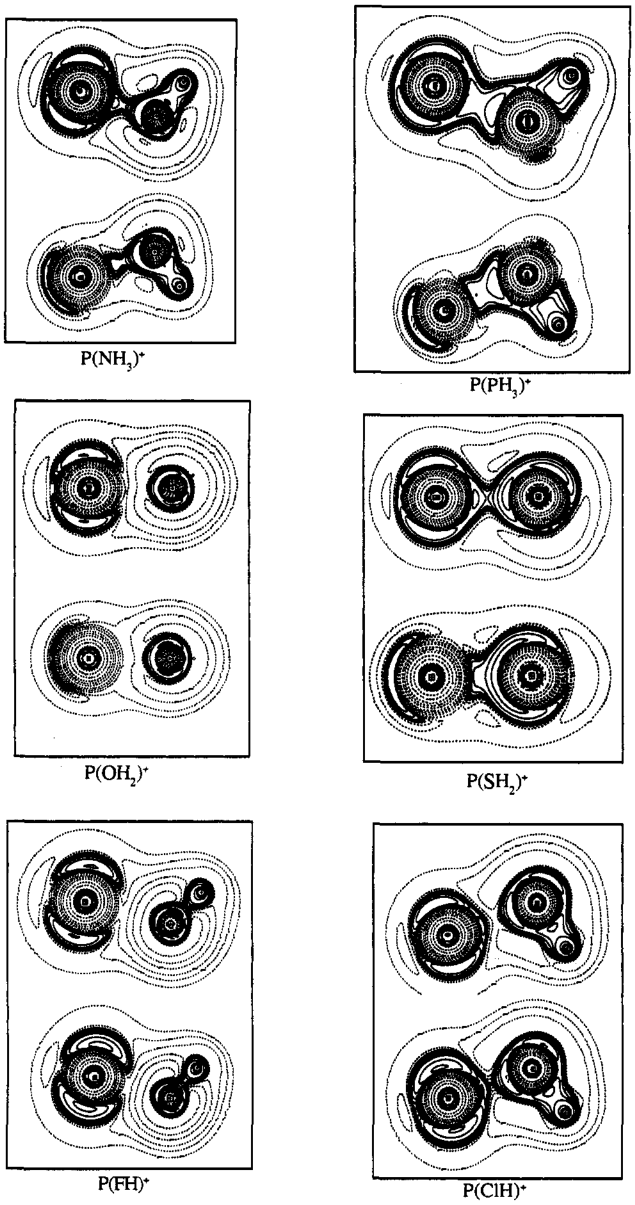


Figure 4. MP2/6-31G(d) geometries for singlet two-ligand ion−molecule complexes. Distances are in Å and angles in degrees.

respectively ($I = E_{P^{+2}} - E_{P^+}$; $A = E_{P^+} - E_P$). For the triplet P^+, doublet P^{+2} and quadruplet P were considered for the calculation of I and A, respectively. For the calculation of η corresponding to singlet P^+, doublet P^{+2} and doublet P were employed.

3. Results

3.1. Geometries. Optimized geometries of the one-ligand ion−molecule complexes are in agreement with the expected general features of an ion−molecule complex. Thus, intramolecular parameters are only slightly modified with respect to the values of the free molecules. However, the ion−ligand distances vary substantially among the various ligands investigated (see Figures 1 and 2). Notice that for both triplet and singlet states the largest P−X distance is found for the halogens. As a general rule, the P−X distances obtained for the singlet states are shorter than those found for the triplets, whereas the X−H distances increase accordingly. The largest differences between triplet and singlet P−X distances are observed for P−O



$P(NH_3)^+$ $P(PH_3)^+$ $P(OH_2)^+$ $P(SH_2)^+$ $P(FH)^+$ $P(ClH)^+$

Figure 5. Contour maps of the $\nabla^2\varrho$'s of the PL^+ one-ligand ion–molecule complexes for L = NH_3, OH_2, FH, PH_3, SH_2 and ClH, in both triplet (top) and singlet (bottom) states. Negative values of $\nabla^2\varrho$ are denoted by solid contours, positive values by dotted contours. For PXH_3^+ and PXH^+ systems, the P–X–H plane is considered, and for PXH_2^+, the σ_v symmetry plane.

Table 6. Ion–Molecule Bond Properties for the One-Ligand Complexes[a]

species		D_e	R	$\varrho(r_c)$	$\nabla^2\varrho(r_c)$	$H(r_c)$
$P(NH_3)^+$	$^3A_2$	−85.80	1.915	0.1073	0.0241	−0.0808
	$^1A'$	−86.43	1.894	0.1110	0.0668	−0.0840
$P(OH_2)^+$	$^3A''$	−57.90	1.889	0.0897	0.1083	−0.0553
	$^1A_1$	−64.84	1.785	0.1032	0.3150	−0.0604
$P(FH)^+$	$^3A''$	−28.73	1.955	0.0681	0.0933	−0.0307
	$^1A'$	−29.13	1.905	0.0748	0.1028	−0.0379
$P(PH_3)^+$	$^3A_2$	−84.33	2.224	0.1110	−0.1394	−0.0638
	$^1A'$	−86.66	2.163	0.1224	−0.1793	−0.0782
$P(SH_2)^+$	$^3A''$	−66.78	2.254	0.0949	−0.0695	−0.0501
	$^1A_1$	−76.89	1.951	0.1309	0.1936	−0.1079
$P(ClH)^+$	$^3A''$	−40.91	2.280	0.0766	−0.0022	−0.0350
	$^1A'$	−47.33	2.129	0.0987	−0.0379	−0.0706

[a] D_e is in kcal/mol and R in Å. $\varrho(r_c)$, $\nabla^2\varrho(r_c)$, and $H(r_c)$ are in atomic units.

Table 7. Ion–Molecule Bond Properties for the Two-Ligand Complexes[a]

species		D_e	R	$\varrho(r_c)$	$\nabla^2\varrho(r_c)$	$H(r_c)$
$P(NH_3)_2^+$	$^3A_{2g}$	−18.49	2.196	0.0657	0.0519	−0.0209
	$^1A_1$	−55.10	1.924	0.1011	0.0686	−0.0727
$P(OH_2)_2^+$	^3A	−19.56	2.110	0.0608	0.0940	−0.0176
	$^1A_1$	−36.79	1.892	0.0875	0.1162	−0.0531
$P(FH)_2^+$	^3B_g	−15.08	2.122	0.0500	0.1128	−0.0107
	^1A	−18.23	1.968	0.0668	0.0940	−0.0288
$P(PH_3)_2^+$	$^3A''$	−5.80	3.377	0.0129	0.0285	+0.0006
			2.271	0.1011	−0.1002	−0.0523
	$^1A_1$	−70.48	2.148	0.1190	−0.1646	−0.0824
$P(SH_2)_2^+$	^3B_g	−10.69	2.609	0.0483	0.0414	−0.0092
	$^1A_1$	−44.66	2.187	0.1026	−0.0910	−0.0666
$P(ClH)_2^+$	^3A	−10.38	2.575	0.0414	0.0647	−0.0052
	^1A	−25.09	2.259	0.0774	0.0057	−0.0369

[a] D_e is in kcal/mol and R in Å. $\varrho(r_c)$, $\nabla^2\varrho(r_c)$, and $H(r_c)$ are in atomic units.

and P–S bonds. Change in the point group between triplets and singlets is also observed. Thus, for XH_2 systems, the complexes change from C_s in the triplet state to a planar C_{2v} in the singlet, and for $P(XH_3^+)$ systems, from the C_{3v} in the former to the C_s in the latter.

Differences between the geometries of the singlet and triplet states of two-ligand complexes are more pronounced. In the triplet states, we find linear complexes with P–X distances much larger than the corresponding distances of the one-ligand complexes. Also, the intramolecular geometries are closer to the values of the free ligand. The two ligands attached to the ion are found to be equivalent, except for the $P(PH_3)_2^+$ complex. In this complex, one of the ligands is bonded to the ion at a distance similar to that of the one-ligand case and the other ligand lies much further, namely at 3.377 Å. Instead, singlet states present angular complexes with an X–P–X angle around 90°. However, all of them have equivalent ligands and the P–X distances are closer to those of the one-ligand complexes.

3.2. Energies. Base level, G1, and G2 energies, along with the corrections made to the base energy, are shown in Tables 1 and 2. For one-ligand complexes, the largest corrections correspond to ΔE^{2df} and ΔE^{ZPE}. Also notice that ΔE^{2df} and ΔE^{qci} corrections are more pronounced in the singlet states than in the triplets, while the remaining corrections are of similar magnitude. For the two-ligand complexes, the corrections due to ΔE^{2df} and ΔE^{qci} dominate again. As for the one-ligand complexes, ΔE^{2df} is higher in the singlet state than in the triplet, however ΔE^{QCI} is of similar magnitude. Not great differences are encountered between the singlet and triplet ΔE^+ and Δ corrections.

Energy gaps between the singlet and triplet states are reported in Table 3 at three levels of theory: base, G1, and G2. Inspection of Table 3 reveals that the agreement between G1 and G2 theory is kept within 2 kcal/mol and all of the one-ligand complexes have triplet ground states. The largest gap corresponds to FH, and it decreases following the order: FH > NH_3 > PH_3 > ClH > OH_2 > SH_2. For the two-ligand complexes, the ground state is either triplet or singlet, depending on the ligand attached to the ion. Thus, PH_3, SH_2, and NH_3 present singlet ground states, whereas FH, ClH, and OH_2 have triplet ones. It should be pointed out that the G1 theory predicts a singlet ground state for OH_2, whereas the G2 predicts a triplet ground state.

3.3. Dissociation Energies. For one-ligand complexes, G1 and G2 dissociation energies are in agreement within 2 kcal/mol. The largest correction to the base energy is due to the ΔE^{2df} contribution. For singlet states, ΔE^{QCI} corrections are remarkable too, while in the triplet case, they are of lesser importance. It should be pointed out that binding energies are always greater for singlet than for triplet states, denoting the

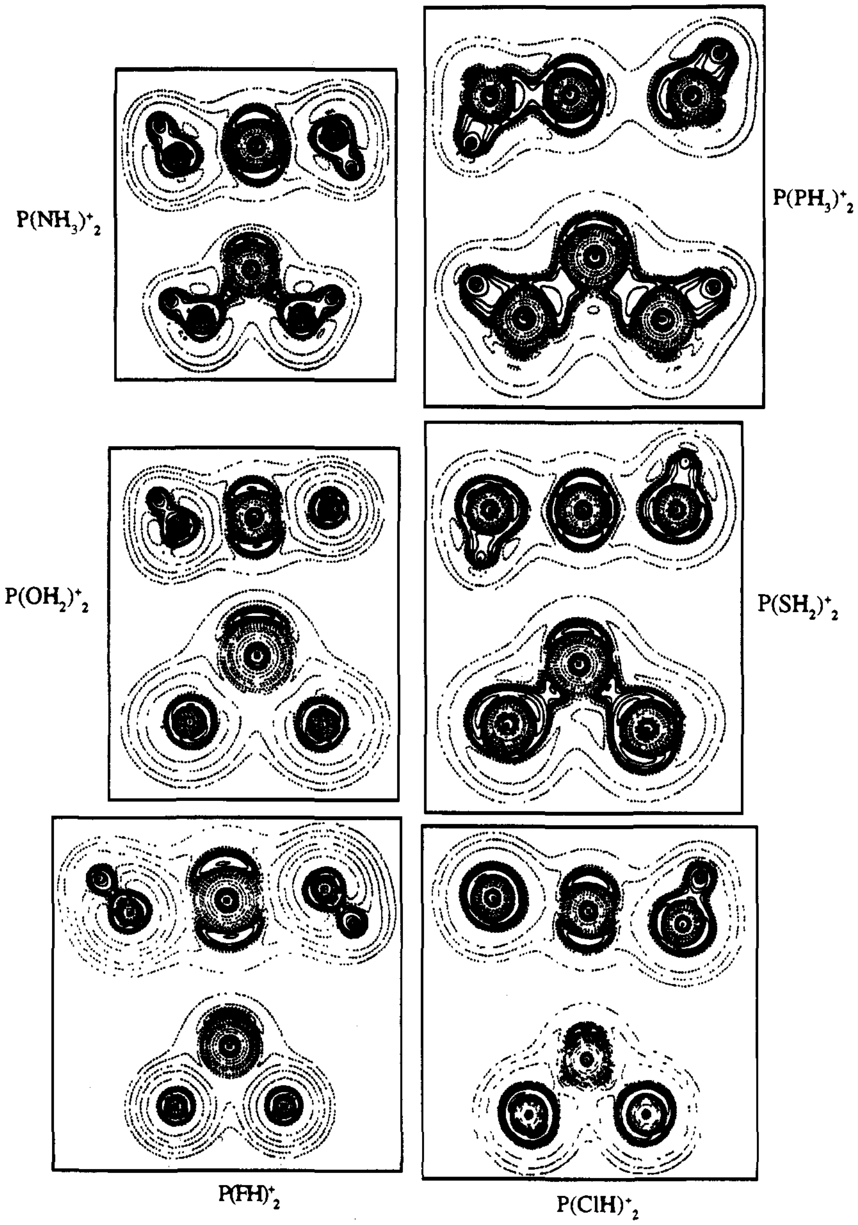


Figure 6. Contour maps of the $\nabla^2\varrho$'s of the PL_2^+ two-ligand ion–molecule complexes for L = NH_3, OH_2, FH, PH_3, SH_2, and ClH, in both triplet (top) and singlet (bottom) states. Negative values of $\nabla^2\varrho$ are denoted by solid contours, positive values by dotted contours. For triplet systems, the X–P–X–H plane is considered, and for singlets, the X–P–X plane.

stronger ion–ligand interaction of the singlet states. This effect is more pronounced for OH_2, SH_2, and ClH, which accounts for the lower singlet–triplet gap encountered in these complexes.

For two-ligand complexes, the agreement between G1 and G2 D_e's is maintained within 2 kcal/mol, except for the singlet $P(SH_2)^+$ complex (2.51 kcal/mol). The ΔE^{2df} correction loses some of its importance for the triplets while it remains important for the singlets, and ΔE^{QCI} corrections present the same behavior as for the one-ligand complexes. The D_e's for the singlets now are much larger than for the triplets. The difference is maximum for PH_3 and then descends along the following order: $PH_3 > NH_3 > SH_2 > OH_2 > ClH > FH$. This enhanced ion–molecule interaction of the singlet state makes PH_3, NH_3, and SH_2 to have singlet ground states, since it is able to overcome the gap between triplet and singlet phosphorus ion (25.20 kcal/mol). For the remaining ligands, it is not big enough and their triplet state continues being the ground state.

3.4. Atomic Charges. Mulliken, natural, and Bader charges have been calculated for the one-ligand complexes. In our previous studies,[3,4] we found a nice agreement between natural and Bader charges, whereas Mulliken charges tend to describe more covalent bonds and, subsequently, to render lower values of the charge on the phosphorus (Q_P). In general, this behavior is also observed for the systems treated here. A large amount of the positive charge is beared out by the phosphorus, as it corresponds to an ion–molecule situation. As we move to the right on the periodic table, larger Q_P's are obtained. Also the Q_P's are found to be larger for first-row hydrides than for second-row ones. Exceptions to this rule are PH_3 and SH_2, for which larger charges are obtained for the triplets than for the singlets.

For some systems, we have found abnormaly large Bader charges. For instance, $P(PH_3)^+$ has a charge of 2.304 on the phosphorus of the phosphine. Clearly, this is too high to be realistic, and in our opinion, it is the result of a deficiency of the method. Other authors have reported similar problems with the Bader charges,[16] which have been attributed to the so called "tail effect". Natural charges seem to overcome this difficulty and give more reasonable values for the $P(PH_3)^+$ system.

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Table 8. Mulliken, Natural, and Bader Charges for the One-Ligand Complexes

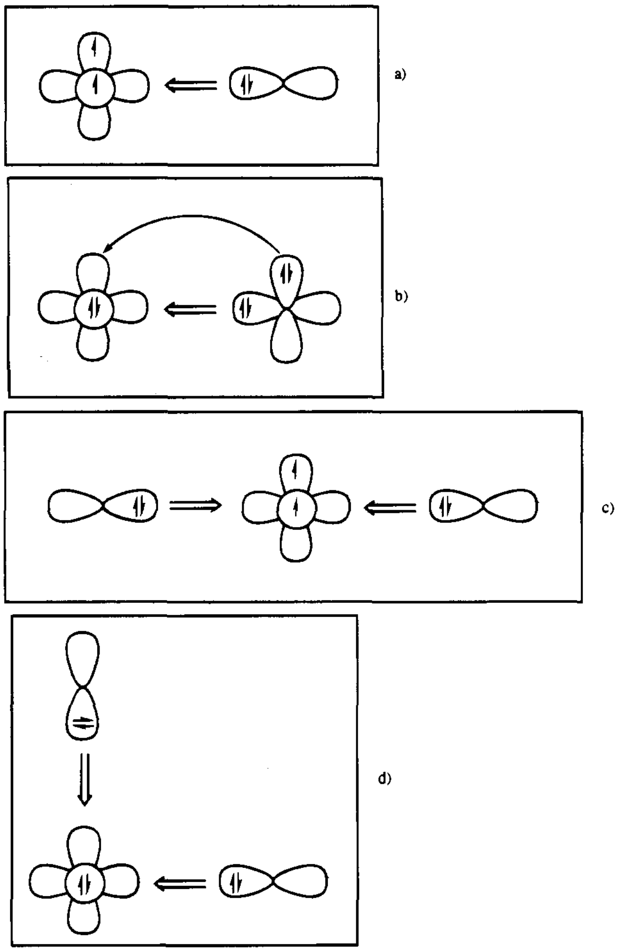
species	spin	atom	Mulliken	natural	Bader
$P(NH_3)^+$	$^3A_2$	P	0.567	0.672	0.742
		N	−0.552	−0.991	−1.171
		H	0.328	0.440	0.476
	$^1A'$	P	0.560	0.671	0.747
		N	−0.554	−0.999	−1.185
		H_1	0.327	0.450	0.480
		H_2	0.334	0.439	0.479
$P(OH_2)^+$	$^3A''$	P	0.692	0.776	0.830
		O	−0.479	−0.891	−1.198
		H	0.394	0.557	0.684
	$^1A_1$	P	0.649	0.746	0.832
		O	−0.476	−0.889	−1.230
		H	0.414	0.572	0.699
$P(FH)^+$	$^3A''$	P	0.807	0.859	0.896
		F	−0.250	−0.489	−0.677
		H	0.443	0.630	0.781
	$^1A'$	P	0.778	0.834	0.878
		F	−0.229	−0.470	−0.661
		H	0.451	0.636	0.784
$P(PH_3)^+$	$^3A_2$	P	0.312	0.402	0.432
		P	0.396	0.398	2.070
		H	0.097	0.067	−0.501
	$^1A'$	P	0.343	0.427	0.455
		P	0.371	0.382	2.034
		H_1	0.097	0.085	−0.479
		H_2	0.094	0.053	−0.505
$P(SH_2)^+$	$^3A''$	P	0.402	0.497	0.546
		S	0.245	0.113	0.211
		H	0.177	0.195	0.121
	$^1A_1$	P	0.441	0.505	0.811
		S	0.174	0.111	−0.133
		H	0.193	0.192	0.161
$P(ClH)^+$	$^3A''$	P	0.583	0.648	0.690
		Cl	0.150	0.029	−0.079
		H	0.267	0.323	0.389
	$^1A'$	P	0.516	0.589	0.703
		Cl	0.219	0.101	−0.085
		H	0.265	0.309	0.382

Table 9. Natural Charges for the Two-Ligand Complexes[a]

species	spin	Q_P	Q_X	Q_H
$P(NH_3)_2^+$	$^3A_{2g}$	0.631	−1.014	0.400
	$^1A_1$	0.348	−0.930	$0.434^{(H_1)}$ $0.411^{(H_2)}$
$P(OH_2)_2^+$	^3A	0.743	−0.907	0.517
	$^1A_1$	0.526	−0.848	0.543
$P(FH)_2^+$	^3B_g	0.834	−0.514	0.602
	^1A	0.625	−0.468	0.620
$P(PH_3)_2^+$	$^3A''$	0.399	$0.370^{(P_1)}$ $0.051^{(P_2)}$	$0.059^{(H_1,H_2)}$ $0.001^{(H_3,H_4)}$
	$^1A_1$	−0.180	0.492	$0.064^{(H_1)}$ $0.017^{(H_2)}$
$P(SH_2)_2^+$	^3B_g	0.424	−0.042	0.165
	$^1A_1$	0.033	0.137	0.173
$P(ClH)_2^+$	^3A	0.609	−0.103	0.299
	^1A	0.300	0.049	0.301

[a] See Figures 3 and 4 for the numbering of the atoms.

Scheme 1. Schemes of the Molecular Orbital Interactions between the Ion and the Ligand for (a) Triplet One-Ligand Complexes, (b) Singlet One-Ligand Complexes, (c) Triplet Two-Ligand Complexes, and (d) Singlet Two-Ligand Complexes



For the above-mentioned reason and because of the lower computational cost, we have calculated only natural charges for the two-ligand complexes. The observed trends can be summarized as follows. Lower Q_P's are obtained for two-ligand complexes than for one-ligand ones. The singlets have much lower Q_P's than the triplet states. The dependency of the Q_P's with respect to the ligand is similar to that found for the one-ligand complexes. Thus, as we move to the right on the periodic table, Q_P increases and decreases when we pass from a first-row hydride to its corresponding second-row one.

4. Discussion

4.1. One-Ligand Complexes. One-ligand ion−molecule complexes have been found to have triplet ground states, with the hydride bond corresponding to a shared interaction in which its bond properties are slightly changed from those of the free ligands. Ion−ligand bonds can be understood as the result of two different binding mechanisms: one electrostatic, in which the bond is due, in a first approximation, to the attraction between a positive point of charge and the dipole of the ligand, and second an electronic binding mechanism, in which orbital interactions are responsible for the bond. P^+ is an open shell ion with empty orbitals of low energy, suitable for accepting electrons from the lone pairs of the ligands. Hence, electronic effects are expected to play an important role in the bonding of PL_n^+ systems. An idea of the strength of such electronic effects can be obtained from the analysis of $H(r_c)$. All of the complexes show negative values of $H(r_c)$, denoting that some covalency enhances the bond. Although these values are much lower than those of typical covalent interactions,[14] they do not correspond to a situation of purely electrostatic bonds, for which positive values of $H(r_c)$ are expected. Also, the values of Q_P are lower than +1, denoting that some electron donation is taking place. The electronic interactions for the triplet ground states can be understood (Scheme 1a) in terms of the partial donation of the

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(15) NBO Version 3.1: Glendening, E. D.; Reed, A. E.; Carpenter, J. E. and Weinhold, F.

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electron lone pair of the ligand to the empty p orbital of P^+ lying along the bond axis. Due to these electronic effects, the values of the D_e's are larger than expected from a purely electrostatic binding mechanism. Values for ion–molecule complexes of closed shell ions, in which electronic effects are minor, are much lower. For instance, in the case of $M^+(OH_2)$ systems (M being Na and K), the experimental values[17] of D_e are 24.0 and 17.0 kcal/mol, and for $M^+(NH_3)$, 21.4 and 13.2 kcal/mol, respectively.

Inspection of the shape of the Laplacian, along with the values of $H(r_c)$, reveals that the degree of electron donation is highly ligand dependent. Attending to the shape of the Laplacian, the bonds can be classified into two categories. Thus, for OH_2 and FH, the Laplacians show a closed shell form,[18] for which regions of electronic charge depletion are connecting the P and X basins. The Laplacian of the intramolecular subsystem is only slightly deformed with respect to that of the free ligand, denoting the rigidity of the electronic cloud of these ligands. Despite this rigidity, electron donation still exists (notice the negative values of $H(r_c)$), and in agreement with the donation in Scheme 1, one lone pair (a maximum of the $-\nabla^2\varrho(r)$) is pointing toward a hole in the valence shell of charge concentration of the phosphorus.

Opposite to this behavior, the $-\nabla^2\varrho(r)$'s of NH_3, PH_3, and SH_2 show hints common to shared interactions.[19] Now the electron donation is so strong that we find a zone of electronic charge concentration linking the two nuclei, and instead of one maximum belonging to the lone pair, we find two maxima bound by a saddle point. Naturally, now the electronic cloud of the ligand is more deformable, hence it allows for a more effective donation. Correspondingly, the ligands are more strongly bonded to the ion than in the previous two cases (see Table 4), hence Q_P's are lower. ClH shows an intermediate situation: two maxima and a saddle point appear in the internuclear region, but the saddle point has positive values of the Laplacian.

The ligand dependency of the bond is reflected in the great variation of Q_P's and D_e's for the various complexes (from +0.402 for PH_3 to +0.859 for FH, and from a value of 85.80 kcal/mol for NH_3 to 28.73 kcal/mol for FH). The stability of the triplet one-ligand complexes seems to be governed by the electron donating ability of the ligand. The stability order of the first- and second-row hydrides in $NH_3 > OH_2 > FH$ and $PH_3 > SH_2 > ClH$, respectively, just the order in which the covalency decreases (see values of $H(r_c)$). Also, we have found that P^+ bonds preferentially to the softest bases in XH_2 and XH systems. Thus, larger D_e's are obtained for second-row hydrides. This behavior is in agreement with the consideration of P^+ as a soft acid.[21–23] The hardness (η) of the triplet P^+ is 4.61 eV, a very low value compared with the values of closed shell ions, i.e., 21.08 eV for Na^+ and 13.64 for K^+.[20] According to the Pearson's HSAB principle,[19–21] a soft acid prefers to be bonded to soft bases, for which electronic effects are favored, rather than to hard ones, for which electrostatic attraction dominates. The exception occurs for XH_3 systems: P^+ is more strongly bonded to the ammonia than to phosphine, though only by 1.47 kcal/mol. Clearly, electrostatic effects are still important, and the larger donation of phosphine is compensated by the larger dipole of the ammonia. We would also like to point out that comparison of the values of $H(r_c)$ between elements belonging to different rows to establish the strength of the donation must be done with caution. For instance, OH_2 presents a more negative value of $H(r_c)$ than SH_2 but it is clear that SH_2 has a larger sharing of electron density than water.

The singlet state constitutes the first excited spin state for all of the one-ligand complexes. The main consequence of the change of the spin state is that another empty p orbital on the P^+ is now suitable of accepting electrons (Scheme 1b). Therefore, an additional π donation is likely to take place and, hence, to strengthen the bond. Subsequently, larger D_e's are observed for the singlet complexes than for the triplets, $H(r_c)$'s present lower values, and the ion–molecule distances are reduced with respect to the triplet states. This enhancement of the covalency for the singlet states is specially favored for ligands that have additional lone pairs to donate (SH_2, OH_2, and ClH; *FH* is too rigid to support any π donation). For example, SH_2 exhibits an increase of 10 kcal/mol of its D_e and the absolute value of $H(r_c)$ is increased by a factor of 2. In spite of this enhancement of the binding energy, it is not enough to make the singlet state more stable than the triplet. It should be taken into account that the triplet–singlet gap of the P^+ is 25 kcal/mol, larger than the energy gained by the bond stabilization.

The trend of preferency for ligands is kept similar to that of the triplet state, except that now P^+ shows greater affinity for phosphine than for ammonia. Subsequently, the results are now in full agreement with the HSAB principle, i.e., the soft acid P^+ prefers to be bonded to the softest bases in all the cases. It should be emphasized that the P^+ singlet is softer than the triplet ($\eta_{\mathrm{singlet}} = 4.24$ eV), and this is reflected in the increased difference of the binding energies between hard and soft bases.

4.2. Two-Ligand Complexes. The two-ligand complexes have triplet or singlet ground states, depending upon the nature of the ligand. Complexes of PH_3, SH_2, and NH_3 have singlet ground states, whereas OH_2, ClH, and FH have triplet ones. The characteristics of the ion–molecule bond depend on the spin state under consideration. For triplets, linear complexes with large P–X distances are found. The D_e's obtained for them are much lower than in the one-ligand case and more similar to the values of other ion–molecule complexes of closed shell ions. By contrast, singlet ion–molecule complexes present an angular form with ion–ligand distances and D_e's closer to the values of the corresponding one-ligand complexes. Let us discuss the model of binding in these spin states.

For the triplets, the empty p orbital of the P^+ has been already partially occupied with the lone pair of the first ligand. The PL^+ system has two options for accepting a new ligand: First, to lose some of the charge donated by the P–X bond and share it with the second ligand (Scheme 1c), and second, to not change the P–X bond and form a purely electrostatic bond with the new ligand. Both possibilities lead to linear complexes, in which the two ligands adopt an anti-periplanar conformation, in spite of the large distance between them, as it can be appreciated in the Newman projections depicted in Figure 3.

Except PH_3, all the ligands prefer the first possibility. Thus, two equivalent P–ligand bonds are obtained, in which the covalency of each bond has been dramatically decreased with respect to the bond in one-ligand complexes. As it can be seen in Figure 6, the Laplacians for P–N, P–S, and P–Cl have lost some of their previous characteristics of shared interactions and the absolute values of $H(r_c)$ are decreased with respect to the values of the corresponding one-ligand complexes (compare

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(17) Reference 2, pp 1016 and 1041.

(18) Reference 12, p 293.

(19) Reference 12, p 290.

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Tables 6 and 7). From the above considerations, it is clear that now electrostatic effects have a greater dominance in the binding mechanism. The loss of part of the covalency in the P−X bond makes the D_e's decrease to values similar to those of closed shell ions and elongates the P−ligand distances. The global donation to P^+ is slightly augmented, and somewhat lower Q_P's than in the one-ligand complexes are obtained.

Phosphine is the only case in which the second possibility occurs. Two different P−P bonds are obtained. One of them presents characteristics of shared interactions and it is strongly bonded to the P^+, while the other shows characteristics of closed shell behavior. Positive values of $H(r_c)$ are obtained, indicating that electronic effects are not present in this bond and that electrostatic effects completely dominate the bond. Correspondingly, two very different P−P distances are observed, 2.271 and 3.377 Å, and a very low D_e value of 5.80 kcal/mol is obtained for the second ligand. It should be pointed out that the great electron donation through the P−P bond makes the P^+ ion lose most of its positive charge, and hence, the electrostatic binding is weakened considerably.

The higher electrostatic character of the bond explains the trend of the stability in the new bonds. Now, unlike the one-ligand complexes, larger D_e's are obtained for first-row hydrides than for second-row ones and the stability order within the same row does not correspond with the order of $H(r_c)$. For example, water is bonded stronger than NH_3, although the absolute value of $H(r_c)$ is lower for the former than for the latter.

In its singlet state, P^+ has two p orbitals suitable of accepting electrons. As we have mentioned, in one-ligand complexes, one of them has been employed to support a σ donation while the other bears a weaker π donation. When a second ligand bonds, the π donation is lost in order to allow for an additional σ donation with the new ligand (Scheme 1d). Therefore, angular complexes are obtained, for which σ donation is present for each ligand. The nature of the bond is now maintained for the situation observed for one-ligand complexes. Thus, although some covalency is lost (notice that absolute values of $H(r_c)$ are lower), the decrease is not enough to change the nature of the ion−ligand bond (look at the Laplacian in Figure 6). Hence, PH_3, SH_2, and NH_3 maintain characteristics of shared interactions and the absolute value of $H(r_c)$ for all of the ligands is much larger than for the triplets. Accordingly, the bond in the singlet states is stronger than in the triplets; therefore, the P−X distances are shorter and closer to the values of the one-ligand complexes. Unlike triplet complexes, the trend in singlet complex stability is explained from electronic considerations. Second-row hydrides are bonded stronger than first-row ones, and as we go to the right within each row, larger D_e's are obtained. Also, the global donation to the P^+ is highly augmented and Q_P's much lower than for triplet complexes are found for the singlet complexes. Finally, it is also interesting to note that in these singlet two-ligand complexes the conformations adopted by both ligands are those that minimize the electrostatic and steric repulsion between them. In addition, as would be expected from electronic effects corresponding to covalent bonds, the more electronegative the X atom, the lower the X−P−X angle (see Figure 4), the only exception being the $P(ClH)_2^+$ complex.

5. Concluding Remarks

Both triplet and singlet P^+ behave as soft acids. This agrees with the HSAB principle that states that soft acids prefer to be bonded to the softest bases, for which electronic effects are favored. The trend in D_e's, the shape of the Laplacian, and the values of $H(r_c)$ support these considerations. The only exception is due to the preference of the triplet P^+ to bond to NH_3 rather than to PH_3. Larger stability is encountered for singlet one-ligand complexes than for triplet ones, although triplets are the ground state.

Two-ligand complexes present very different behavior, depending on the spin state. Thus, for singlet states, electronic effects maintain their importance and the trends in stability between different ligands are similar to those of the one-ligand complexes. However, in the triplets, electronic effects are less important and, subsequently, a greater lowering of D_e's is observed. The trend in ligand stability cannot now be explained solely by arguments based on the differences of the electron donation ability of the ligands. Our calculations demonstrate that differences in the charge-multipole electrostatic potential should also be taken into account.

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