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Structure, Reaction Enthalpies, Entropies, and Free Energies of Cation−Molecule Complexes. A Theoretical Study by Means of the ab Initio Complete Basis Set CBS-Q Method

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Ab initio molecular orbital calculations at the CBS-Q level of theory have been performed for 72 complexes in order to determine the effects of molecular structure on gas-phase basicity toward H^+, Li^+, and Mg^{2+}. It is shown that basicities toward metal cations Li^+ and Mg^{2+} differ considerably from the corresponding gas-phase basicities toward H^+. Calculated interaction energies vary as $H^+ \gg Mg^{2+} > Li^+$. The relative basicities of the bases studied depend characteristically on type of cation and coordination site.

1. Introduction

Improvements in computers, numerical computer programs, and theoretical methods are making ab initio calculations including electron correlation increasingly available for small and even moderately large molecules.[1,2] Recent developments in quantum chemistry resulted in theoretical models (Gaussian-1 (G1) and Gaussian-2 (G2) theories introduced by John Pople and co-workes[3,4] and complete basis set (CBS) methods developed by George Petersson and several collaborators[5−7]), able to predict properties of neutral molecules and ions within so-called chemical accuracy (about 2 kcal mol^{-1}). This makes these procedures extremely useful in thermochemical studies.

Metal cations such as lithium, sodium, potassium, magnesium, calcium, and others take part in many important processes.[8,9] Most of these metal-related chemical processes pertain to interactions with biological molecules. The accurate estimation of interaction energies between the ions and the carrier molecules can help our understanding of proper function of these systems (e.g., ion channels, metalloproteins, and metalloenzymes).

The addition of a proton to the base represents the simplest chemical reaction. However, this reaction plays an important part in many chemically and biologically relevant processes and has been the subject of extensive experimental studies and theoretical investigations.[10−20] The nature of the bond formed by the Lewis acid H^+ with the ligand is quite different in comparison with binding of metal ions.[21,22]

Important information on cation-base interactions can be obtained by investigation of thermodynamics of this process in the gas phase, which is free of solvent and counterion influences. The intrinsic enthalpies and Gibbs energies of these reactions establish useful Lewis basicity orders in the absence of solvent. The bond enthalpies and Gibbs energies corresponding to the reaction 1, where M^{n+} is a small cation (Li^+, Na^+, K^+, etc.) and L a Lewis base have been measured in the gas phase for a number of complexes.[23−28]

$$M^{n+}(g) + L(g) \rightarrow ML^{n+}(g) \qquad (1)$$

The experimental conditions of measurements do not allow us to determine energetics of this process for all chemically and biologically interesting bases. That is, the ion-equilibrium method is not well suited[29] for systems with high bond enthalpies (i.e., larger than ∼40 kcal mol^{-1}), but many ion−ligand complexes can have such high bond enthalpies particularly when multiply charged ions are involved.[30] Ab initio theoretical methods can in principle provide a wealth of information inaccessible by current experimental techniques. The computed interaction energies for cation−base complexes at Hartree−Fock level are slightly exaggerated in comparison with the exact experimental values (usually by several kilocalories per mole), and it is necessary to apply a semiempirical correction to obtain satisfactory agreement.[31]

The aim of the present work is to provide a reliable set of gas-phase energies for the interaction of small cations (H^+, Li^+, and Mg^{2+}) with selected Lewis bases. These values are used for the determination of an absolute scale of basicity for these compounds.

2. Computational Details

The geometry of complexes L···M, where M = H^+, Li^+, and Mg^{2+}, and L denotes the Lewis bases investigated (Figure 1) has been completely optimized at MP2/6-31G(d) level within the CBS-Q theory.[5,6,7,32] The gas-phase basicity was defined as the enthalpy of protonation (ΔH^{298}) for reaction 2.

$$B(g) + H^+(g) \rightarrow BH^+(g) \qquad (2)$$

The enthalpy of protonation, ΔH^{298}, was computed using eqs 3 and 4,

$$\Delta H^{298} = \Delta E^{298} + \Delta(pV) \qquad (3)$$

$$\Delta E^{298} = E^{298}(BH^+) - [E^{298}(B) + {}^3/_2\, RT] \qquad (4)$$

where E^{298} stands for the total energies of bases and their cations

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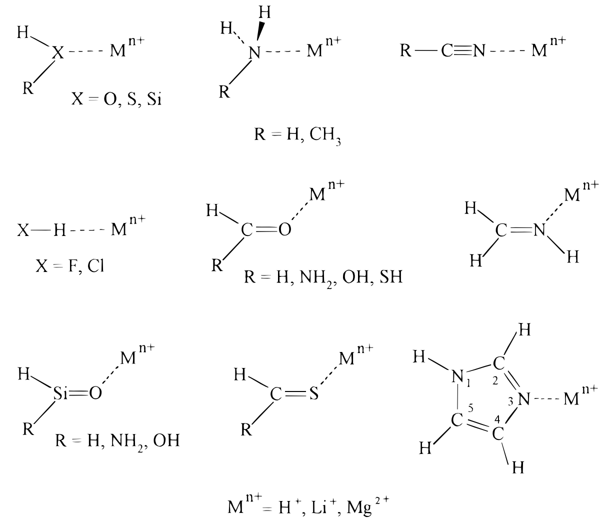


Figure 1. Structure of the cation − Lewis base complexes studied

(including thermal energy correction at $T = 298.15$ K). In eq 3 we substituted $\Delta(pV) = -RT$ (one mol of gas is lost in the reaction 2).

The interaction enthalpy ΔH^{298} for the metal ion−Lewis base complexes is given by the following equation

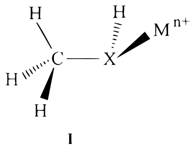
$$\Delta H^{298} = \{E^{298}(\mathrm{BM}^{n+}) - [E^{298}(\mathrm{B}) + E^{298}(\mathrm{M}^{n+})]\} + \Delta(pV) \qquad (5)$$

$$\mathrm{M}^{n+} = \mathrm{Li}^{+} \text{ and } \mathrm{Mg}^{2+}$$

where $E^{298}(\mathrm{M}^{n+})$ and E^{298}(ligand) are the energies of the metal cation and ligand molecules, respectively, and $E^{298}(\mathrm{M}^{n+}\cdots$ligand) is the energy of the complex corrected for thermal energy at $T = 298.15$ K. For the work term in eq 5 we substituted $\Delta(pV) = -RT$. Ab initio calculations were carried out with the aid of the GAUSSIAN94 package of computer codes.[33]

Results and Discussion

3.1. Structure and General Energetic Considerations. The total energies of all calculated species are listed in Table 1. The fully optimized geometries of the complexes under study are given in Table 2. An analysis of the harmonic vibrational frequencies at the HF/6-31G(d) level of theory of the optimized species revealed that both monomers and the HF/6-31G(d) optimized complexes are minima (no imaginary frequencies). Minima were found for the pyramidal $H_2X\cdots H^+$ ($X = O$ or S) complexes; in the case of $CH_3XH_2^+$ (X = O, S, and Si), CH_3SHM^{n+} (Li^+ and Mg^2), and CH_3SiHMg^{2+} systems, staggered structures of type **I** have been computed. For the rest of the complexes studied the minima correspond to the planar C_S structures.



I

The changes of geometry of ligands with complexation can be summarized as follows:

(1) Hard bases, where the donor atom is F, O, or N, form much shorter metal−ligand bonds than the compounds where the donor atom is Si, S, or Cl (soft bases). (2) Substitution of the parent bases results in changes of equilibrium $X\cdots M^{n+}$ distances. For this change both polarization and steric effects of substituent are responsible. (3) Increased unsaturation on the basic center of the parent molecules leads to larger changes of equilibrium $X\cdots M^{n+}$ distances for hard bases than for "soft" molecules (e.g., H_2S and $H_2C{=}S$) (Table 2). (4) The equilibrium distances $X\cdots M^{n+}$ ($M^{n+}{=}H^+$, Li^+, and Mg^{2+}) increase in the order $d(X\cdots H^+) \ll d(X\cdots Li^+) \leq d(X\cdots Mg^{2+})$. Exceptions are the HCl and HCS(OH) bases where the optimum $X\cdots Li^+$ length was computed to be slightly longer than that for the $X\cdots Mg^{2+}$ distance (Table 2). This ordering well correlates with the magnitude of the ionic radii for Li^+ (0.60 Å) and Mg^{2+} (0.65 Å), ref 34. The geometry of the Lewis bases changes only slightly upon complexation. The coordination of the proton and bivalent Mg^{2+} cation exhibits a comparable and large influence. The angles $R{-}X\cdots M^{n+}$ (R = H, CH_3; X = N, O, S, and Si) and $X{=}Y\cdots M^{n+}$ (X=C and Si; Y = O,S,N) under which Lewis acids approach the corresponding base depend strongly on the character of the cation and the electronic structure on the basic center. For so-called sp^3 bases (hydrides and their methyl derivatives), the $R{-}X\cdots M^{n+}$ angle was found to be within a relatively narrow interval, and slightly decreases upon methyl substitution (Table 2). The coordination of a proton to the bases studied leads to more "perpendicular" $R{-}X\cdots H^+$ bond angles than in the corresponding metal ion complexes. A different situation was observed for the $HF\cdots M^{n+}$ and $HCl\cdots M^{n+}$ complexes (Table 2). While the coordination of the hard base HF by hard Lewis acids leads to considerable fluctuations of the $H{-}F\cdots M^{n+}$ bond angles (this bond angle was found in the $HF\cdots Mg^{2+}$ system to be 58° higher than in the H_2F^+ complex), the complexation of the soft base HCl with the same cations is connected with only slight opening of the bond angle (the $HCl\cdots Mg^{2+}$ bond is about 11° larger than the $H{-}Cl\cdots H^+$ angle in the H_2Cl^+ system). The different geometrical arrangement of the $HF\cdots M^{n+}$ and $HCl\cdots M^{n+}$ complexes studied could be explained by the different character of bonding of these two bases. By pairing of hard base with hard acid the ionic interactions will dominate in the $HF\cdots M^{n+}$ systems. The increasing size of coordinated cations (and also higher charge of +2 on Mg) results in a better alignment of the metal cations to the direction of the H−F dipole axis. With the cations studied the more polarizable soft base HCl forms bonds which are more covalent (see also the section Electronic Structures) which results in more rigid $HCl\cdots M^{n+}$ structures (Table 2). The computed $C{=}O\cdots M^{n+}$ and $Si{=}O\cdots M^{n+}$ angles in the formaldehyde and silanone complexes with Li^+ and Mg^{2+} equal 180°, and the metal cations lie on the axis of the double bond. Substitution of one hydrogen by NH_2, OH, and SH groups results in a considerable tilt away from the X=O (X = C or Si) axis (Table 2). This tilt is due to the combined effect of particular changes of atoms of the X=O group and substituents. Similar, but much smaller effects were found recently from ab initio calculations upon methyl substitution of these aldehydes.[35,36] Protonation of formaldehyde, silanone, and their substituted derivatives occurs on one of the oxygen lone pairs. The complexation of both sp^2 and sp hybridized nitrogen in N-bases also follows the lone pair directionality. The binding of the sulfur in the compounds containing an unsaturated C=S bond gives planar C_S structures with trans orientation of the cations with respect to the substituent (Table 2). The large observed differences in the orientation of cations by their coordination to the >C=O and >C=S groups were explained on the basis of different electrostatics.[36]

3.2. Gas-Phase Interaction Energies. Table 3 contains the ab initio CBS-Q interaction enthalpies, entropies, and Gibbs

TABLE 1: Total Energies (in Hartrees) of the Systems Studied (at 298 K)

species	enthalpy	free energy
Li^+	−7.233 480	−7.248 580
Mg^{2+}	−198.820 634	−198.837 483
H_2O	−76.332 697	−76.354 051
H_2S	−398.929 679	−398.952 987
H_2Si	−290.160 619	−290.184 133
NH_3	−56.455 321	−56.477 118
$H_2O\cdots H^+$	−76.591 745	−76.614 775
$\cdots Li^+$	−83.618 136	−83.644 312
$\cdots Mg^{2+}$	−275.277 215	−275.304 585
$H_2S\cdots H^+$	−399.195 129	−399.219 844
$\cdots Li^+$	−406.197 134	−406.225 727
$\cdots Mg^{2+}$	−597.865 978	−597.895 454
$H_2Si\cdots H^+$	−290.471 193	−290.496 088
$\cdots Li^+$	−297.430 879	−297.459 616
$\cdots Mg^{2+}$	−489.124 251	−489.154 039
$H_3N\cdots H^+$	−56.778 274	−56.801 683
$\cdots Li^+$	−63.748 390	−63.774 951
$\cdots Mg^{2+}$	−255.424 051	−255.451 860
CH_3OH	−115.534 016	−115.560 981
CH_3SH	−438.147 026	−438.175 793
CH_3SiH	−329.399 083	−329.428 524
CH_3NH_2	−95.662 498	−95.689 752
$CH_3OH\cdots H^+$	−115.817 789	−115.845 845
$\cdots Li^+$	−122.824 864	−122.855 945
$\cdots Mg^{2+}$	−314.499 340	−314.531 743
$CH_3SH\cdots H^+$	−438.438 674	−438.467 904
$\cdots Li^+$	−445.422 584	−445.455 781
$\cdots Mg^{2+}$	−637.108 313	−637.142 392
$CH_3SiH\cdots H^+$	−329.733 355	−329.765 338
$\cdots Li^+$	−336.679 017	−336.712 947
$\cdots Mg^{2+}$	−528.391 225	−528.426 308
$CH_3NH_2\cdots H^+$	−96.002 959	−96.029 557
$\cdots Li^+$	−102.958 532	−102.989 324
$\cdots Mg^{2+}$	−294.645 711	−294.677 669
HF	−100.355 759	−100.375 433
HCl	−460.343 773	−460.364 937
HCN	−93.282 723	−93.305 510
CH_3CN	−132.520 837	−132.548 341
$HF\cdots H^+$	−100.536 731	−100.558 942
$\cdots Li^+$	−107.624 136	−107.649 587
$\cdots Mg^{2+}$	−299.262 649	−299.286 248
$HCl\cdots H^+$	−460.553 218	−460.576 557
$\cdots Li^+$	−467.601 694	−467.629 549
$\cdots Mg^{2+}$	−659.248 525	−659.277 384
$HCN\cdots H^+$	−93.553 017	−93.574 229
$\cdots Li^+$	−100.572 113	−100.597 848
$\cdots Mg^{2+}$	−292.246 402	−292.273 720
$CH_3CN\cdots H^+$	−132.815 264	−132.844 279
$\cdots Li^+$	−139.821 798	−139.854 399
$\cdots Mg^{2+}$	−331.515 771	−331.549 206
$H_2C=O$	−114.338 925	−114.364 349
$H_2C=S$	−436.933 487	−436.959 656
$H_2Si=O$	−365.382 251	−365.408 849
$H_2C=N(H)$	−94.460 045	−94.485 784
$H_2C=O\cdots H^+$	−114.606 803	−114.632 651
$\cdots Li^+$	−121.627 160	−121.657 023
$\cdots Mg^{2+}$	−313.301 399	−313.331 917
$H_2C=S\cdots H^+$	−437.222 562	−437.249 961
$\cdots Li^+$	−444.206 316	−444.237 585
$\cdots Mg^{2+}$	−635.890 354	−635.922 430
$H_2Si=O\cdots H^+$	−365.698 693	−365.726 779
$\cdots Li^+$	−372.698 843	−372.729 980
$\cdots Mg^{2+}$	−564.409 035	−564.440 989
$H_2C=N(H)\cdots H^+$	−94.788 469	−94.813 928
$\cdots Li^+$	−101.756 343	−101.785 721
$\cdots Mg^{2+}$	−293.442 623	−293.472 994
$NH_2(H)C=O$	−169.647 129	−169.676 689
$NH_2(H)C=S$	−492.235 383	−492.265 443
$NH_2(H)Si=O$	−420.714 303	−420.745 077
$NH_2(H)C=O\cdots H^+$	−169.961 323	−169.990 099
$\cdots Li^+$	−176.957 024	−176.989 601
$\cdots Mg^{2+}$	−368.663 436	−368.696 574
$NH_2(H)C=S\cdots H^+$	−492.557 438	−492.588 001
$\cdots Li^+$	−499.527 947	−499.562 454
$\cdots Mg^{2+}$	−691.244 235	−691.279 729
$NH_2(H)Si=O\cdots H^+$	−421.050 701	−421.082 303
$\cdots Li^+$	−428.042 776	−428.077 274
$\cdots Mg^{2+}$	−619.765 688	−619.800 936
HCOOH	−189.521 421	−189.549 556
HCS(OH)	−512.102 129	−512.131 602
HSiOOH	−440.602 531	−440.632 762
HCO(SH)	−512.106 204	−512.136 221
$H(OH)C=O\cdots H^+$	−189.800 820	−189.829 249
$\cdots Li^+$	−196.812 622	−196.844 835
$\cdots Mg^{2+}$	−388.497 633	−388.530 545
$H(OH)C=S\cdots H^+$	−512.393 292	−512.423 446
$\cdots Li^+$	−519.377 920	−519.412 022
$\cdots Mg^{2+}$	−711.072 199	−711.107 158
$H(OH)Si=O\cdots H^+$	−440.923 387	−440.954 660
$\cdots Li^+$	−447.921 594	−447.955 762
$\cdots Mg^{2+}$	−639.635 650	−639.670 994
$H(SH)C=O\cdots H^+$	−512.396 247	−512.426 297
$\cdots Li^+$	−519.399 458	−519.433 466
$\cdots Mg^{2+}$	−711.095 643	−711.130 187
imidazole (Im)	−225.833 376	−225.864 337
$Im\cdots H^+$	−226.189 992	−226.221 020
$\cdots Li^+$	−233.145 737	−233.180 145
$\cdots Mg^{2+}$	−424.860 947	−424.896 259

energies of the systems investigated. For comparison, the available experimental vapor-phase thermodynamic data[37] are also included in this table. The enthalpies and Gibbs energies of these complexes vary with no exceptions as $H^+ > Mg^{2+} > Li^+$. Thus the proton is the stronger Lewis acid than the monovalent and bivalent metal ions studied. The magnesium cation, because of its higher charge of +2, is bonded substantially more strongly to the Lewis bases than the lithium cation (Table 3).

The first- and second-row hydrides investigated represent the simplest Lewis bases which involve single-bonded basic centers. The substitution of the hard basic atom (O or F) by a soft one (S or Cl) causes an increase of the basicity toward H^+. The metal ions Li^+ and Mg^{2+} exhibit higher binding affinity toward hard acids H_2O and HF compared to soft acids H_2S and HCl (Table 3). For hydride−M^{n+} ($M^{n+} = H^+$, Li^+, and Mg^{2+}) complexes the basicity order is H^+ as acid, N: > Si: > S: > O: > Cl: > F:; Li^+ as acid, N: > O: > Si: > S: > F: > Cl:; Mg^{2+} as acid, N: > Si: > O: > S: > F: > Cl:. Methyl substitution leads to an increase of the basicity. This increase is, however, not regular and for coordination of Mg^{2+} cation a different ordering of basicities was observed (the methylsilene acts as the strongest base and the basicity decreases as follows: Si: > N: > O: > S:).

A second category of complexes are the bases which contain C═O, C═S, C═N(H) and Si═O groups, respectively. The softening effect of unsaturation causes, besides the changes in the geometry of the complexes discussed in the previous section, also considerable changes in their thermodynamics (Table 3). The increased polarizability of bases due unsaturation results in substantially greater reaction enthalpies and Gibbs energies in the $=X\cdots M^{n+}$ (X = N, O, and S; $M^{n+} = H^+$, Li^+, and Mg^{2+}) systems in comparison to the $-X\cdots M^{n+}$ complexes. The importance of polarization effects on the interaction energy of these systems is demonstrated by the complexes of ammonia, methanimine and, imidazole. The aromatic system of imidazole is more polarizable than the unsaturated isolated C═N bond of methanimine and therefore acts as a better electron donor (stronger base). That is, the proton affinity of imidazole is 21.1 kcal mol^{-1} higher than the value for NH_3 and 17.7 kcal mol^{-1}

TABLE 2: MP2/6-31G(d)-Optimized Geometries of the Ion−Base Systems Investigated[a]

	H_2O				H_2S				H_2Si				NH_3			
parameter		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}
d_{X-H}	0.962	0.980	0.967	0.980	1.339	1.347	1.342	1.352	1.518	1.456	1.488	1.475	1.014	1.026	1.021	1.031
$d_{X\cdots M^{n+}}$		0.980	1.859	1.947		1.347	2.449	2.459		1.456	2.654	2.689		1.026	2.014	2.081
<HXH	105.9	114.8	107.0	106.3	93.4	96.1	95.5	96.8	92.6	120.0	102.2	116.6	107.0	109.5	105.6	104.8
<HXM		114.8	126.5	126.9		96.1	104.4	101.7		120.0	128.9	121.7		109.5		

	CH_3OH				CH_3SH				CH_3SiH				CH_3NH_2			
		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}
d_{X-H}	0.964	0.978	0.967	0.976	1.341	1.346	1.342	1.351	1.524	1.469	1.493	1.478	1.016	1.026	1.022	1.029
d_{X-C}	1.418	1.510	1.459	1.523	1.818	1.824	1.829	1.851	1.909	1.825	1.865	1.832	1.466	1.511	1.497	1.532
d_{C-H}	1.094	1.090	1.092	1.092	1.095	1.095	1.094	1.095	1.095	1.097	1.094	1.094	1.096	1.092	1.094	1.094
$d_{X-M^{n+}}$		0.978	1.844	1.918		1.346	2.421	2.431		1.469	2.640	2.688		1.026	2.011	2.073
<H_xXC	107.8	115.3	108.5	107.4	96.6	100.3	99.2	101.0	94.5	121.5	103.7	117.2	109.5	111.3	107.9	107.3
<XCH_c	106.5	104.5	106.9	106.7	106.6	106.6	106.8	106.9	113.6	112.0	114.3	115.7	109.0	108.3	109.3	109.4
<CXM		115.3	127.2	129.4		100.3	111.7	112.0		121.5	132.2	127.1		111.3	114.2	115.7

	HF				HCl				HCN^b				CH_3CN^b			
parameter		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}
d_{X-H}	0.925	0.976	0.938	0.961	1.280	1.302	1.288	1.305								
d_{X-C}									1.177	1.154	1.171	1.170	1.179	1.159	1.175	1.178
d_{C-H}									1.073	1.087	1.080	1.091	1.095	1.098	1.096	1.099
d_{C-C}													1.467	1.454	1.462	1.452
$d_{X-M^{n+}}$		0.976	1.778	1.876		1.302	2.391	2.378		1.018	1.997	2.020		1.014	1.960	1.979
<CCH													110.1	108.9	109.5	109.2
<HXM		115.5	180.0	173.5		96.6	108.5	107.8								
<CNM										179.1	177.6	177.9		180.0	180.0	180.0

	$H_2C{=}O$				$H_2C{=}S$				$H_2Si{=}O$				$H_2C{=}NH$			
parameter		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}
d_{X-H}	1.110	1.095	1.100	1.102	1.094	1.092	1.092	1.092	1.484	1.466	1.470	1.465	1.025	1.021	1.023	1.027
d_{C-H}													1.094	1.089	1.091	1.091
d_{X-Y}	1.213	1.251	1.226	1.224	1.619	1.623	1.626	1.636	1.542	1.581	1.553	1.590	1.282	1.283	1.288	1.299
$d_{X-M^{n+}}$		0.986	1.838	2.208		1.347	2.441	2.455		0.970	1.782	1.840		1.021	1.993	2.043
<HXY	122.2	121.8	120.7	121.0	122.0	123.0	124.0	126.5	124.1	121.4	121.2	117.9	118.3	119.4	119.6	121.1
<HXH	115.5	123.0	118.7	117.9	116.1	119.6	116.7	117.6	111.6	124.9	117.6	124.2	116.2	121.1	117.6	118.3
<XYM		115.6	180.0	180.0		98.6	107.4	108.7		132.9	180.0	180.0		121.6	128.4	130.0

	$NH_2(H)C{=}O$				$NH_2(H)C{=}S$				$NH_2(H)Si{=}O$			
		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}
d_{X-H}	1.110	1.092	1.099	1.094	1.097	1.092	1.093	1.091	1.480	1.461	1.465	1.460
$d_{X=Y}$	1.217	1.292	1.248	1.289	1.639	1.697	1.673	1.723	1.535	1.586	1.555	1.597
$d_{X-N(O)}$	1.365	1.298	1.325	1.299	1.348	1.306	1.321	1.300	1.690	1.644	1.663	1.645
$d_{X-M^{n+}}$		0.974	1.773	1.829		1.340	2.343	2.344		0.967	1.758	1.822
<H_xXY	123.0	121.7	121.0	119.6	121.4	119.8	122.6	123.6	126.0	123.8	122.6	119.1
<H_xXN	111.9	119.5	115.2	117.8	112.4	116.6	113.9	115.8	106.3	120.1	112.7	118.9
<XYM		113.5	164.3	163.3		94.8	109.8	110.1		132.2	174.9	174.7
<H_xXO												

	HCOOH				HCS(OH)				$HSiO_2H$				HCO(SH)			
parameter		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}		H^+	Li^+	Mg^{2+}
d_{X-H}	1.101	1.093	1.096	1.095	1.094	1.093	1.093	1.094	1.470	1.456	1.459	1.456	1.108	1.096	1.102	1.099
$d_{X=Y}$	1.206	1.275	1.233	1.271	1.624	1.678	1.651	1.698	1.532	1.578	1.549	1.589	1.208	1.287	1.239	1.285
d_{X-O}	1.347	1.265	1.301	1.267	1.335	1.281	1.302	1.272	1.636	1.575	1.600	1.566	1.783	1.665	1.713	1.666
d_{O-H}	0.973	0.985	0.977	0.983	0.975	0.981	0.979	0.987	0.965	0.969	0.966	0.968	1.342	1.348	1.344	1.347
$d_{X-M^{n+}}$		0.979	1.818	1.864		1.343	2.393	2.380		0.968	1.772	1.832		0.979	1.810	1.847
<H_xXY	125.6	123.5	123.5	121.8	124.0	121.6	124.5	125.0	127.2	124.6	123.6	119.6	123.9	120.5	120.8	118.9
<XYM		114.8	158.8	159.9		94.7	108.3	109.0		134.3	174.3	175.6		113.7	161.2	159.3
<XOH	106.5	114.1	110.9	116.0	107.4	116.1	125.3	123.5	119.1	132.5	128.6	141.9	93.9	95.3	95.2	96.5
<H_xCS													110.7	117.2	113.0	114.6
<H_xXO	109.0	115.9	111.7	113.7	109.4	112.8	110.2	111.5	104.5	115.4	109.2	114.7				

	imidazole			
parameter		H^+	Li^+	Mg^{2+}
d_{1-2}	1.367	1.341	1.351	1.337
d_{2-3}	1.326	1.341	1.341	1.360
d_{3-4}	1.377	1.376	1.386	1.400
d_{4-5}	1.383	1.376	1.378	1.374
d_{1-5}	1.376	1.376	1.374	1.375
$d_{N\cdots M}$		1.017	1.951	1.987
<1−2−3	111.9	106.8	110.4	108.8
<2−3−4	104.7	110.3	105.8	106.7
<3−4−5	111.1	106.4	109.7	108.3
<2−1−5	107.3	110.3	108.9	110.3
<4−3-M		125.5	125.0	124.6

[a] Geomtries: angles in degrees and distances in angstroms. [b] The H−C≡N and C−C≡N angles were found to be equal to 180°.

TABLE 3: Calculated Gas-Phase Enthalpies ΔH, Entropies, ΔS, and Gibbs Energies, ΔG, of the Cation Coordinated Systems

	ΔH (kcal mol^{-1})		ΔS (cal deg^{-1} mol^{-1})	ΔG (kcal mol^{-1})	
complex	exptl[a]	calcd	calcd	exptl	calcd
$H_2O\cdots H^+$	−165.2	−164.1	3.4		−165.1
$\cdots Li^+$	−34.0[b]	−33.2	−21.5	−27.3[b]	−26.8
$\cdots Mg^{2+}$		−78.3	−22.5		−71.6
$H_2S\cdots H^+$	−168.5	−168.1	3.0		−169.0
$\cdots Li^+$		−21.9	−20.5		−15.8
$\cdots Mg^{2+}$		−73.2	−22.5		−66.5
$H_2Si\cdots H^+$		−196.4	3.0		−197.3
$\cdots Li^+$		−23.7	−20.8		−17.5
$\cdots Mg^{2+}$		−90.3	−22.1		−83.7
$NH_3\cdots H^+$	−204.1	−204.2	3.4		−205.2
$\cdots Li^+$	−39.1[b]	−38.0	−21.8	−32.1[b]	−31.5
$\cdots Mg^{2+}$		−93.5	−22.5		−86.8
$CH_3OH\cdots H^+$	−180.3	−179.5	2.7		−180.3
$\cdots Li^+$	−38.1[b]	−36.6	−23.1	−30.3[b]	−29.7
$\cdots Mg^{2+}$		−91.4	−23.9		−84.3
$CH_3SH\cdots H^+$	−184.8	−184.5	1.0		−184.8
$\cdots Li^+$		−25.5	−17.5		−20.3
$\cdots Mg^{2+}$		−88.9	−24.3		−81.6
$CH_3SiH\cdots H^+$		−211.2	5.7		−212.9
$\cdots Li^+$		−29.7	−22.2		−22.9
$\cdots Mg^{2+}$		−108.2	−23.6		−101.1
$CH_3NH_2\cdots H^+$	−214.9	−215.2	−1.6		−214.7
$\cdots Li^+$	−41.1[b]	−39.9	−24.3	−33.3[b]	−33.2
$\cdots Mg^{2+}$		−102.6	−25.6		−95.6
$HF\cdots H^+$	−115.7	−115.1	5.3		−116.7
$\cdots Li^+$		−22.5	−19.8		−16.6
$\cdots Mg^{2+}$		−54.6	−27.2		−46.6
$HCl\cdots H^+$	−133.1	−132.9	4.3		−134.2
$\cdots Li^+$		−16.2	−18.5		−10.7
$\cdots Mg^{2+}$		−53.7	−20.5		−47.6
$HCN\cdots H^+$	−170.4	−171.1	3.4		−170.1
$\cdots Li^+$	−36.4[b]	−35.6	−25.2	−28.7[b]	−28.1
$\cdots Mg^{2+}$		−90.3	−25.5		−82.7
$CH_3CN\cdots H^+$	−186.2	−186.3	3.0		−187.2
$\cdots Li^+$		−42.9	−20.8		−36.7
$\cdots Mg^{2+}$		−109.8	−21.8		−103.3
$H_2C{=}O\cdots H^+$	−170.4	−169.6	1.0		−169.9
$\cdots Li^+$	−36.0[b]	−35.0	−22.5	−28.2[b]	−28.3
$\cdots Mg^{2+}$		−89.6	−24.5		−82.3
$H_2C{=}S\cdots H^+$	−181.6	−182.9	2.7		−183.7
$\cdots Li^+$		−25.3	−21.2		−19.1
$\cdots Mg^{2+}$		−86.1	−22.8		−79.4
$H_2Si{=}O\cdots H^+$	−201.0	−200.1	−0.3		−201.0
$\cdots Li^+$		−53.1	−23.5		−46.1
$\cdots Mg^{2+}$		−130.3	−25.2		−122.8
$H_2C{=}N(H)\cdots H^+$	−203.8	−207.6	−0.7		−207.4
$\cdots Li^+$		−40.0	−24.1		−32.8
$\cdots Mg^{2+}$		−102.2	−25.5		−94.6
$NH_2(H)C{=}O\cdots H^+$	−196.5	−198.6	−1.3		−198.2
$\cdots Li^+$		−48.5	−25.4		−41.0
$\cdots Mg^{2+}$		−123.4	−27.9		−115.1
$NH_2(H)C{=}S\cdots H^+$		−203.6	−1.0		−203.9
$\cdots Li^+$		−38.0	−23.4		−31.0
$\cdots Mg^{2+}$		−119.0	−21.8		−112.5
$NH_2(H)Si{=}O\cdots H^+$		−212.6	1.7		−213.1
$\cdots Li^+$		−60.5	−24.8		−53.1
$\cdots Mg^{2+}$		−145.7	−27.2		−137.6
$H(OH)C{=}O\cdots H^+$	−177.3	−176.8	0.7		−177.0
$\cdots Li^+$		−37.1	−24.2		−29.9
$\cdots Mg^{2+}$		−98.5	−26.2		−90.7
$H(OH)C{=}S\cdots H^+$		−184.2	1.3		−184.6
$\cdots Li^+$		−26.0	−18.1		−20.6
$\cdots Mg^{2+}$		−94.7	−25.8		−87.0
$H(OH)Si{=}O\cdots H^+$		−202.8	2.3		−203.5
$\cdots Li^+$		−54.6	−24.6		−47.3
$\cdots Mg^{2+}$		−134.2	−25.8		−126.5
$H(SH)C{=}O\cdots H^+$		−183.5	0.0		−183.5
$\cdots Li^+$		−36.9	−19.5		−31.1
$\cdots Mg^{2+}$		−106.9	−27.2		−98.8
$Im\cdots H^+$	−225.2	−225.3	0.0		−225.3
$\cdots Li^+$		−50.4	−25.5		−42.8
$\cdots Mg^{2+}$		−130.8	−27.5		−122.6

[a] For experimental proton affinities see ref 37. [b] Reference 25.

larger than that for $H_2C{=}NH$. These bases show different basicity order toward H^+ and metal cations. The calculated proton affinities increase in the order: $C{=}N$: > $C{=}S$: > $C{=}O$:; thus, the imine group is the most basic and the carbonyl moiety the least basic one. For Li^+ and Mg^{2+} complexes a different order of basicity was found ($C{=}N$: > $C{=}O$: > $C{=}S$:). The different ordering of the basicities of these compounds toward H^+ and metal ions Li^+ and Mg^{2+} could be explained by the effects of ionic charge and size. H^+ penetrates into the electron cloud of donor and forms highly covalent bond. The adhesion of metal ions Li^+ and Mg^{2+} to basic centers is, due to their smaller polarizing effect, much lower and results in the formation of essentially electrostatic bond. The oxygen of the silanone is a stronger base than the one in the formaldehyde. It is known[38,39] that the $Si{=}O$ bond is strongly polarized toward oxygen in comparison to the $C{=}O$ bond and exhibits significantly ionic $^{+}Si{:::}O^{-}$ character. The expected dominance of electrostatic interactions in the systems studied and larger bond dipole and polarizability[38,39] of the $Si{=}O$ bond in comparison with the $C{=}O$ bond should be the main reason for the larger basicity of silanone and its substituted derivatives. The sulfur-by-oxygen substitution in the thiocarbonyl compounds leads (owing to the marginal difference in electronegativities of carbon and sulfur) to a considerable decrease of the polarization of the $C{=}S$ bond in comparison with the $C{=}O$ group and to a decrease of interaction energy of the metal ion−base systems. The protonation leads to a reverse ordering of basicity. The proton affinity of $H_2C{=}S$ was computed to be 13.3 kcal mol^{-1} higher than the one of $H_2C{=}O$ (Table 3). A different polarizing effect of H^+ in the $C{=}O\cdots H^+$ and $C{=}S\cdots H^+$ bonds is apparently responsible for this reverse ordering of the basicity (see also section Electronic Structures). The substitution of one hydrogen in formaldehyde, thioformaldehyde and silanone by electron-donating substituents (OH, NH_2, and SH) results in higher interaction energies. The amino group causes a higher increase of basicity of parent compounds than the OH substituent.

The proton affinity of nitriles (HCN and CH_3CN) was computed to be 33.1 and 28.9 kcal mol^{-1} lower than for the amines (NH_3 and CH_3NH_2). The complexation of the same bases by the lithium and magnesium cations led to a substantially smaller gap (about 2 kcal mol^{-1}) for unsubstituted bases. However, acetonitrile binds more strongly to Li^+ and Mg^{2+} ions than methylamine (Table 3).

As it follows from the present calculations of the basicity order, the 24 bases involved in this study exhibit by coordination to hydrogen, lithium, and magnesium cations different ordering of basicity. No general basicity order was observed (Table 3). To establish whether there is any reasonably general correlation of basicities toward monovalent and bivalent cations in Figure 2, the interaction enthalpies of H^+ vs corresponding ΔH_{Li^+} and $\Delta H_{Mg^{2+}}$ are plotted. From this figure it is evident that there is indeed some general correspondence between the basicities toward Li^+ and Mg^{2+}. A similar weak correlation of the H^+ and Li^+ affinities was also observed experimentally.[28] For the scattering of these basicities (Figure 2), besides the effect of size and charge of cation, the different polarization of hard and soft bases studied is also responsible. The substantially greater basicities toward H^+ has to be also attributed to the stronger covalent binding of H^+.

In real molecular systems the tendency to associate and to react is described by free energies. It is therefore important to know the role of entropy in the binding processes studied. Also listed in Table 3 are the differences in $S°$ values of the complexes

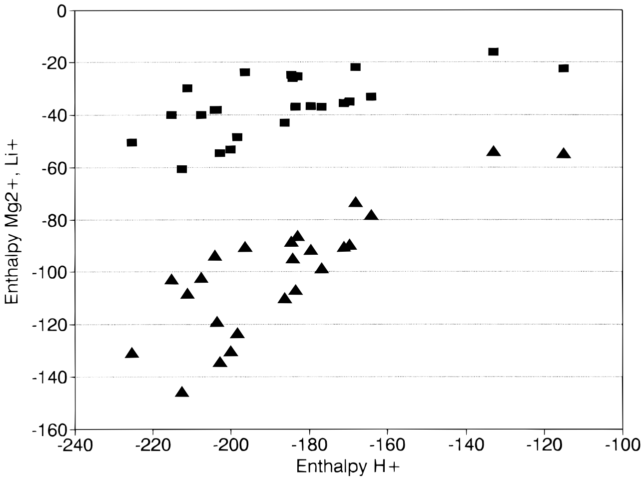


Figure 2. Plot of $\Delta H^0_{\mathrm{Li+}}$ (■) and $\Delta H^0_{\mathrm{Mg2+}}$ (▲) values vs corresponding $\Delta H^0_{\mathrm{H+}}$.

and the isolated species. The computed entropies for the protonation reaction are small (0−6 cal deg^{-1} mol^{-1}). Hence, the effect of entropy on this reaction is very small, and calculated enthalpies and Gibbs energies are very close and follow the same trend in the basicity of species studied. Similar small entropy effects in gas-phase proton transfer were also found experimentally.[40] A different situation was observed for binding of the metal ions Li^+ and Mg^{2+}. The changes in entropy were computed to be substantially larger (about 17−30 cal deg^{-1} mol^{-1}) and negative (Table 3). Large and negative (destabilizing) contributions of entropy reverse the order of exothermicity of the $HF\cdots Mg^{2+}$ and $HCl\cdots Mg^{2+}$ complexes (Table 3). The computed Gibbs energies $\Delta G°$ are negative and span a rather broad energy interval (from −10 to −220 kcal mol^{-1}) meaning that the coordination of the ions studied goes strongly toward the complex formation.

Table 3 contains also the literature data of experimental thermodynamic quantities for clustering of the H^+ and Li^+ ions to selected bases. As it is apparent from this table the CBS-Q method reproduces thermodynamic quantities of the complexes studied within the targeted "chemical" accuracy (within 2.5 kcal mol^{-1}). Most of the computed proton affinities are in excellent agreement with the experimental proton affinities taken from the recent compilation done by Hunter and Lias[37] (NIST Chemistry Web Book). The average deviation between CBS-Q and experimental proton affinities for the 17 compounds is 0.8 kcal mol^{-1}. The largest discrepancy occurs for methanimine for which the experimental value determined by Peerboom et al.[41] (−203.8 kcal mol^{-1}) is by 3.8 kcal mol^{-1} lower than our CBS-Q computed proton affinity (−207.6 kcal mol^{-1}). We obtained exactly the same value of −207.6 kcal mol^{-1} for methanimine using the G2 level of theory[3,4] which is proposed to achieve the "chemical accuracy" of proton affinities.[42] MP4/6-31G** calculations of Del Bene et al.[13] gave an upper limit for proton affinity of methanimine equal to −211.6 kcal mol^{-1}. Accurate results of CBS-Q calculations of additional systems (Table 3) lead to the suggestion that the experimental proton affinity of methanimine may need revision.

A comparison of the CBS-Q computed enthalpies and Gibbs energies for the binding of the lithium cation to selected bases and available experimental values determined by ion cyclotron resonance spectroscopy[25] shows that CBS-Q and experimental data agree within the targeted range of 2 kcal mol^{-1}. To our knowledge, the experimental gas-phase clustering data of Mg^{2+} to Lewis bases and most of the Li^+−base systems have not been measured until now; therefore, our high-level CBS-Q calculations offer a reliable order of basicities of the investigated bases toward these cations.

TABLE 4: Natural Atomic Charges (NAC) and Wiberg Bond Indices (WBI) from the MP2/6-31G(d) NBO Analysis

	NAC		WBI		NAC		WBI
	X	M^{n+}	$X\cdots M^{n+}$		X	M^{n+}	$X\cdots M^{n+}$
H_2O	−0.96			$H_2C{=}O$	−0.58		
$\cdots H^+$	−0.86	0.62	0.614	$\cdots H^+$	−0.61	0.59	0.635
$\cdots Li^+$	−1.10	0.99	0.025	$\cdots Li^+$	−0.82	0.99	0.025
$\cdots Mg^{2+}$	−1.19	1.97	0.061	$\cdots Mg^{2+}$	−0.93	1.97	0.058
H_2S	−0.27			$H_2C{=}S$	0.03		
$\cdots H^+$	0.31	0.23	0.943	$\cdots H^+$	0.50	0.19	0.947
$\cdots Li^+$	−0.43	0.99	0.024	$\cdots Li^+$	−0.12	0.96	0.078
$\cdots Mg^{2+}$	−0.52	1.92	0.146	$\cdots Mg^{2+}$	−0.13	1.76	0.406
SiH_2	0.66			$H_2Si{=}O$	−1.17		
$\cdots H^+$	1.50	−0.17	0.934	$\cdots H^+$	−1.15	0.60	0.639
$\cdots Li^+$	0.55	0.91	0.164	$\cdots Li^+$	−1.40	0.98	0.026
$\cdots Mg^{2+}$	0.70	1.56	0.638	$\cdots Mg^{2+}$	−1.54	1.95	0.089
NH_3	−1.15			$H_2C{=}NH$	−0.66		
$\cdots H^+$	−0.98	0.50	0.574	$\cdots H^+$	−0.72	0.48	0.748
$\cdots Li^+$	−1.29	0.98	0.042	$\cdots Li^+$	−0.93	0.98	0.034
$\cdots Mg^{2+}$	−1.40	1.92	0.157	$\cdots Mg^{2+}$	−1.13	1.92	0.137
CH_3OH	−0.80			$NH_2(H)C{=}O$	−0.70		
$\cdots H^+$	−0.75	0.60	0.635	$\cdots H^+$	−0.71	0.58	0.646
$\cdots Li^+$	−0.96	0.98	0.027	$\cdots Li^+$	−0.95	0.98	0.034
$\cdots Mg^{2+}$	−1.09	1.96	0.079	$\cdots Mg^{2+}$	−1.11	1.96	0.082
CH_3SH	−0.03			$NH_2(H)C{=}S$	−0.22		
$\cdots H^+$	0.50	0.20	0.946	$\cdots H^+$	0.25	0.18	0.951
$\cdots Li^+$	−0.16	0.96	0.068	$\cdots Li^+$	−0.41	0.95	0.088
$\cdots Mg^{2+}$	−0.17	1.79	0.365	$\cdots Mg^{2+}$	−0.42	1.75	0.421
CH_3SiH	0.88			$NH_2(H)Si{=}O$	−1.22		
$\cdots H^+$	1.72	−0.18	0.926	$\cdots H^+$	−1.16	0.59	0.647
$\cdots Li^+$	0.78	0.90	0.173	$\cdots Li^+$	−1.42	0.98	0.037
$\cdots Mg^{2+}$	0.97	1.52	0.664	$\cdots Mg^{2+}$	−1.54	1.95	0.096
CH_3NH_2	−0.94			$H(OH)C{=}O$	−0.69		
$\cdots H^+$	−0.81	0.49	0.754	$\cdots H^+$	−0.70	0.59	0.641
$\cdots Li^+$	−1.10	0.98	0.041	$\cdots Li^+$	−0.92	0.98	0.027
$\cdots Mg^{2+}$	−1.21	1.90	0.181	$\cdots Mg^{2+}$	−1.08	1.96	0.069
HF	−0.56			$H(OH)C{=}S$	−0.15		
$\cdots H^+$	−0.44	0.71	0.481	$\cdots H^+$	0.28	0.20	0.942
$\cdots Li^+$	−0.63	0.99	0.025	$\cdots Li^+$	−0.33	0.96	0.077
$\cdots Mg^{2+}$	−0.70	1.98	0.040	$\cdots Mg^{2+}$	−0.38	1.78	0.385
HCl	−0.28			$H(OH)Si{=}O$	−1.22		
$\cdots H^+$	0.10	0.45	0.793	$\cdots H^+$	−1.17	0.60	0.635
$\cdots Li^+$	−0.34	0.98	0.029	$\cdots Li^+$	−1.43	0.98	0.035
$\cdots Mg^{2+}$	−0.39	1.93	0.139	$\cdots Mg^{2+}$	−1.55	1.95	0.090
HCN	−0.35			$H(SH)C{=}O$	−0.61		
$\cdots H^+$	−0.48	0.55	0.686	$\cdots H^+$	−0.67	0.58	0.649
$\cdots Li^+$	−0.64	0.99	0.020	$\cdots Li^+$	−0.87	0.98	0.028
$\cdots Mg^{2+}$	−0.89	1.96	0.066	$\cdots Mg^{2+}$	−1.07	1.96	0.079
CH_3CN	−0.38			imidazole	−0.55		
$\cdots H^+$	−0.51	0.54	0.696	$\cdots H^+$	−0.58	0.50	0.736
$\cdots Li^+$	−0.68	0.99	0.025	$\cdots Li^+$	−0.81	0.98	0.035
$\cdots Mg^{2+}$	−0.94	1.95	0.078	$\cdots Mg^{2+}$	−1.00	1.92	0.147

3.3. Electronic Structures. The atomic charges of the complexes studied were evaluated by natural population analysis[43−45] using the NBO program.[46] The natural charges (NAC) and Wiberg bond indices (WBI) are shown in Table 4. The coordination of cations considerably increases polarization of Lewis bases, and this polarizing effect of cations is much higher in the case of soft bases containing Si, S, and Cl basic centers. Different effects were, however, observed by adding a proton or the metal ions (Table 4). The protonation of bases leads to a considerable electron transfer toward the H^+ and remarkable change of the electron density at the basic center. For single-bonded basic atoms upon protonation the electron density always decreases. The largest polarization of the $X\cdots H^+$ bonds was found for soft S, Si, and Cl basic centers. In complexes containing unsaturated double bonds the electron density on the hard acid bacic center (O and N) increases with protonation, which is obviously due to the enhancing polarity of the C=X (X = N or O) bonds. The negative charge in the

R(H)C═S···H^+ systems is, owing to the low electronegativity and large polarizability of sulfur, entirely transferred from this atom toward the proton. In the molecules containing the Si═O group, the charge on the oxygen atom is changed only slightly upon protonation, and the entire electron transfer with respect to the high ionic character and polarizability of the Si═O bond[38] comes from the soft silicon atom. The negative "natural" charge on the basic N, O, S, F, and Cl centers upon complexation with the lithium and magnesium cations increases considerably. The silicon positive charge in Li^+ complexes decreases and for Si···Mg^{2+} complexes becomes more positive (Table 4).

The Wiberg bond orders of the H^+−base bonding are very high indicating the entirely covalent character of this bonding. X···H^+ bonds containing soft basic centers (Si, S, and Cl) possess higher covalent character. The bond orders of the Li^+ (Mg^{2+})−base systems were found to be in a rather large interval (0.02−0.6) of values. The binding of hard bases to Li^+ and Mg^{2+} results in low Wiberg bond orders indicating that the covalent bonding of alkali cations to these bases is very weak (i.e., the nature of this bonding is almost electrostatic). A different situation exists for the complexations of hard acids Li^+ and Mg^{2+} to soft Si-, S-, and Cl-bases. The computed Wiberg bond orders of most systems are quite high (0.1−0.6), and these bonds, therefore, possesses considerable covalent character. The covalent character especially increases in the complexes of the more electron-poor magnesium cation (Table 4). For systems with high bond orders the charge transfer from base to the cation is also very large (0.1−0.7 e).

Summary

The interaction enthalpies and Gibbs energies for the 72 complexes between 24 bases and the three cations H^+, Li^+, and Mg^{2+} were computed at the CBS-Q level of theory. The binding energies decrease in the order: $H^+ > Mg^{2+} > Li^+$. The variation in basicity of the parents is significantly changed for the different cations and no general order between proton affinities and adducts of Li^+ and Mg^{2+} was found. The proton affinities vs Li^+ and Mg^{2+} basicities show a nonlinear behavior. The changes in basicities are related to the variation of coordinating atom, the nature of the substituent on the basic center, the polarizability of bases, and the nature of interacting acid. The covalent bond is almost entirely responsible for the formation of protonated complexes. The binding of the Li^+ and Mg^{2+} cations to hard bases (containing N, O, and F basic centers) comes mainly from electrostatic interactions. The covalent character of X···M^{n+} bond ($M^{n+} = Li^+$ or Mg^{2+}) is apparent in complexes with soft bases (containing Si, S, and Cl basic centers). The covalent character of those complexes increases with the increase of the positive charge on alkali metal cation. The CBS-Q method reproduces the thermodynamic quantities of the cation−Lewis base complexes within the "chemical accuracy".

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