

Modulating the intrinsic reactivity of molecules through non-covalent interactions

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Supporting Information (A total of 6 pages)

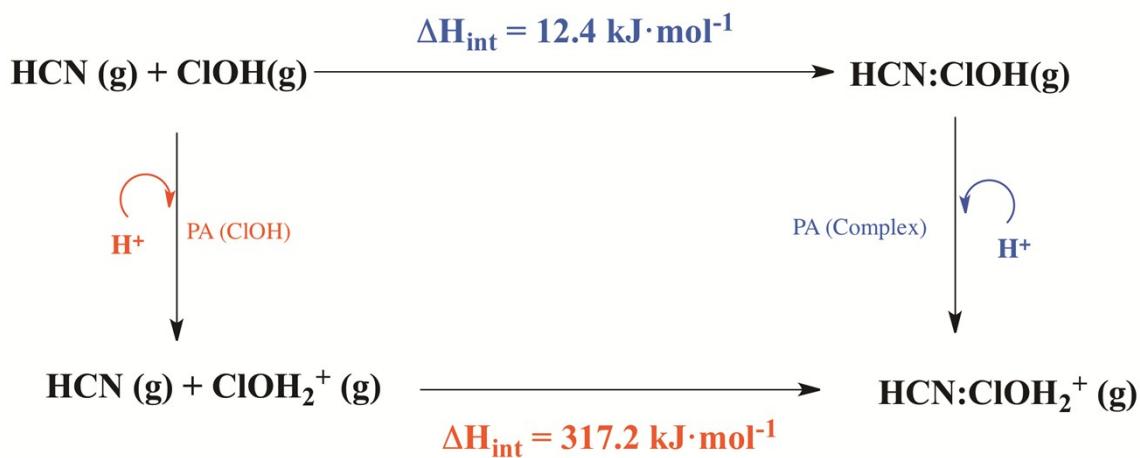
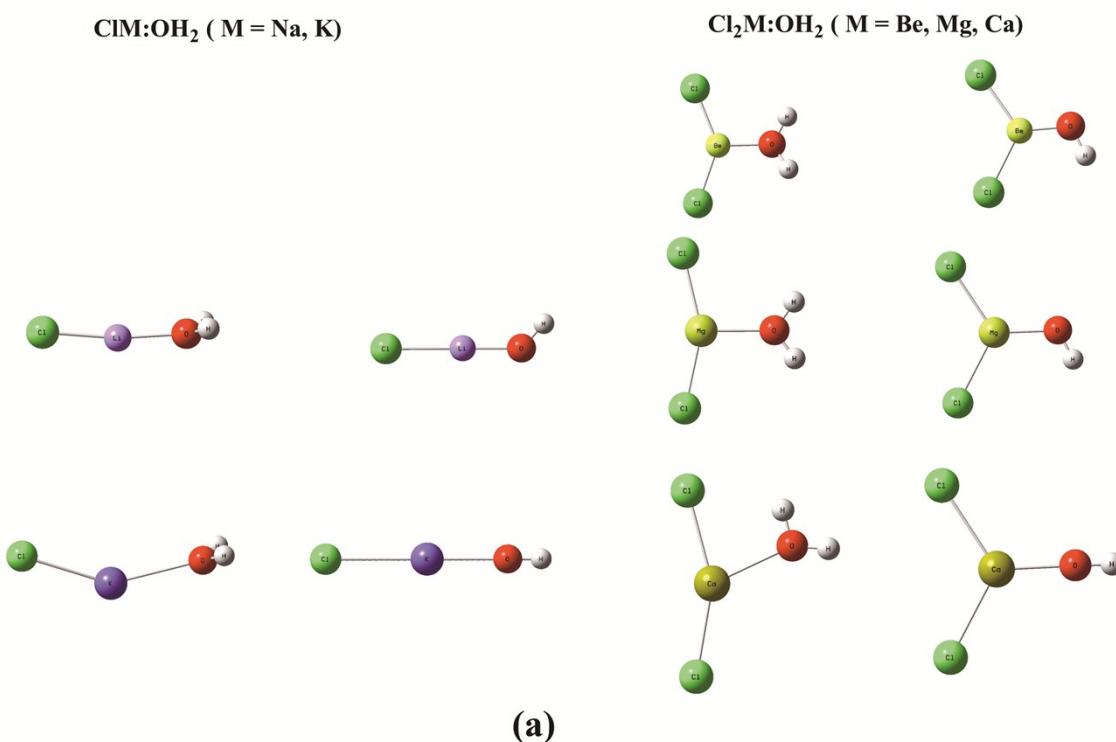
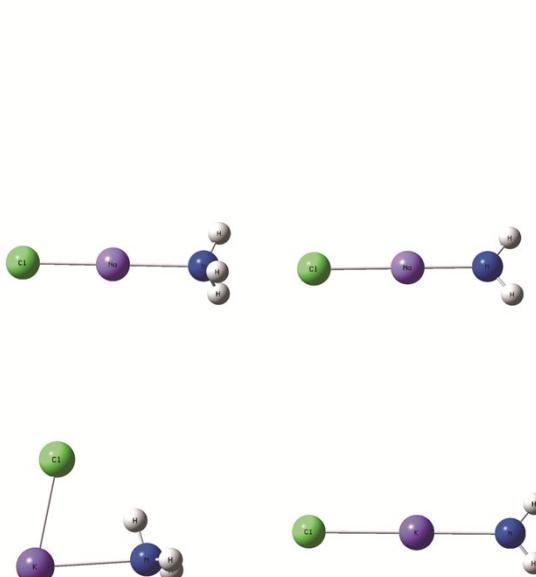
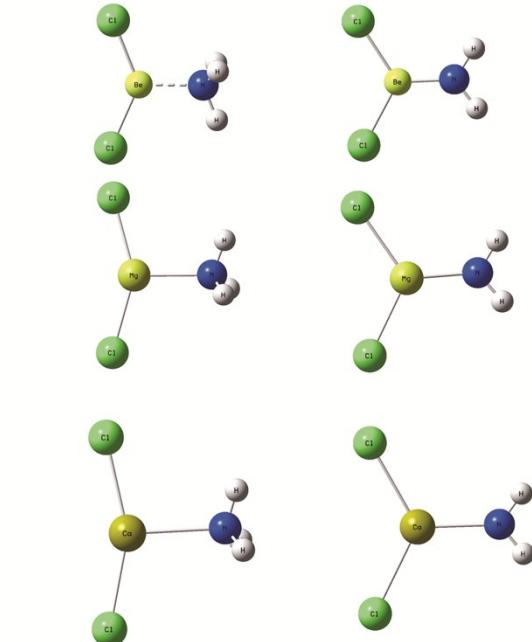
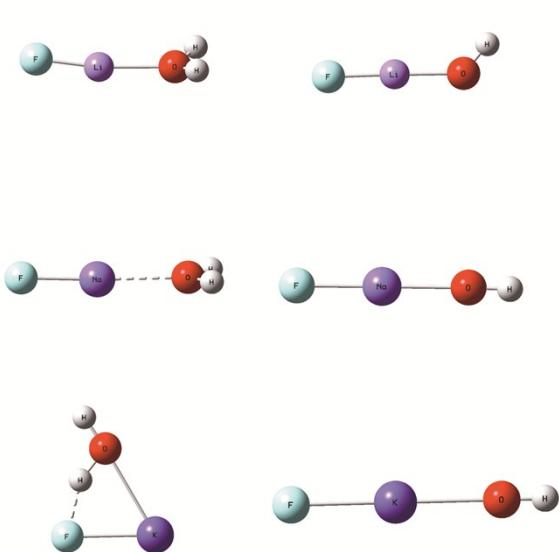
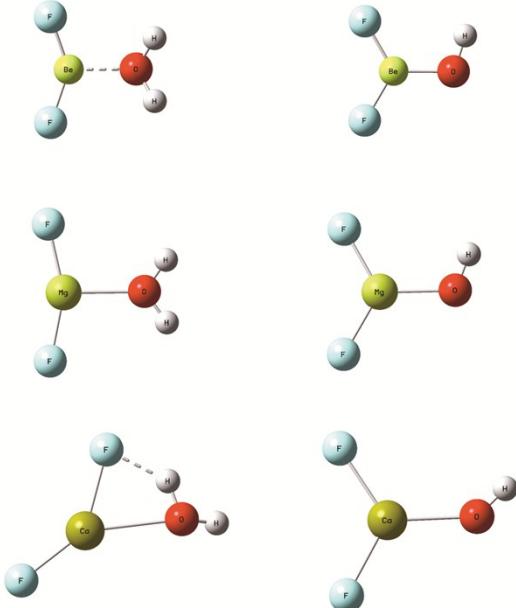


Figure S1. Thermodynamic cycle correlating the Proton Affinity (PA) of the free ClOH molecule and the PA of its complex with HCN with the stabilization of the neutral oxyacid and its protonated form (by association with HCN).



ClM:NH_3 ($\text{M} = \text{Na, K}$) $\text{Cl}_2\text{M:NH}_3$ ($\text{M} = \text{Be, Mg, Ca}$)

(b)

 FM:OH_2 ($\text{M} = \text{Li, Na, K}$) $\text{F}_2\text{M:OH}_2$ ($\text{M} = \text{Be, Mg, Ca}$)

(c)

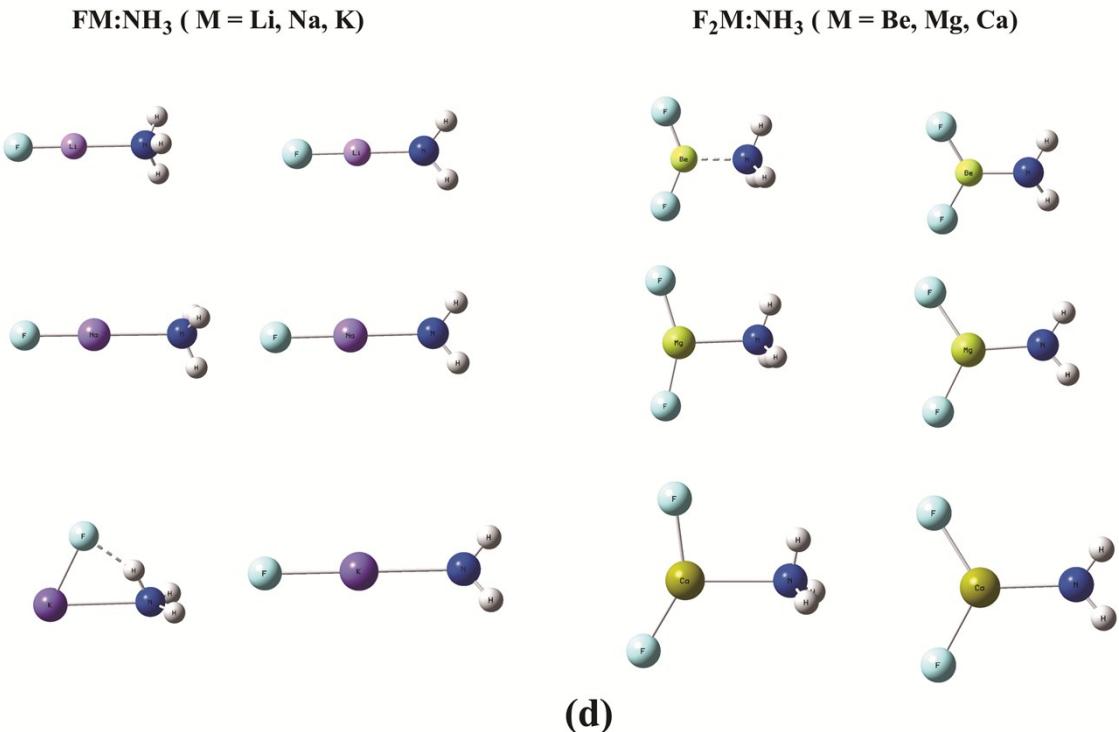


Figure S2. G4 Optimized geometries of the complexes between NaCl, KCl, BeCl₂, MgCl₂ and CaCl₂ with water (**a**) and ammonia (**b**) with, and the complexes between LiF, NaF, KF, BeF₂, MgF₂ and CaF₂ with water (**c**) and ammonia (**d**), and their corresponding deprotonated forms

Table S1. Presence-absence matrix of the Free-Wilson model^a applied to the 24 complexes under investigation

No	Complex	Base	X	Li	Na	K	Be	Mg	Ca	HBs	Minima	Non-minima
1	FLi···OH ₂	0	0	1	0	0	0	0	0	0	-210.8	-210.8
2	FNa···OH ₂	0	0	0	1	0	0	0	0	0	-203.7	-203.7
3	FK···OH ₂	0	0	0	0	1	0	0	0	1	-111.0	-168.6
4	F ₂ Be···OH ₂	0	0	0	0	0	1	0	0	0	-284.5	-284.5
5	F ₂ Mg···OH ₂	0	0	0	0	0	0	1	0	0	-278.9	-278.9
6	F ₂ Ca···OH ₂	0	0	0	0	0	0	0	1	1	-255.8	-266.7
7	ClLi···OH ₂	0	1	1	0	0	0	0	0	0	-241.8	-241.8
8	ClNa···OH ₂	0	1	0	1	0	0	0	0	0	-224.3	-224.3
9	ClK···OH ₂	0	1	0	0	1	0	0	0	0	-202.6	-202.6
10	Cl ₂ Be···OH ₂	0	1	0	0	0	1	0	0	0	-342.1	-342.1
11	Cl ₂ Mg···OH ₂	0	1	0	0	0	0	1	0	0	-314.5	-314.5
12	Cl ₂ Ca···OH ₂	0	1	0	0	0	0	0	1	1	-312.8	-313.2
13	FLi···NH ₃	1	0	1	0	0	0	0	0	0	-187.6	-187.6
14	FNa···NH ₃	1	0	0	1	0	0	0	0	0	-184.5	-184.5
15	FK···NH ₃	1	0	0	0	1	0	0	0	1	-124.2	-151.7
16	F ₂ Be···NH ₃	1	0	0	0	0	1	0	0	0	-254.7	-254.7
17	F ₂ Mg···NH ₃	1	0	0	0	0	0	1	0	0	-262.8	-262.8
18	F ₂ Ca···NH ₃	1	0	0	0	0	0	0	1	0	-249.6	-249.6
19	ClLi···NH ₃	1	1	1	0	0	0	0	0	0	-216.3	-216.3
20	ClNa···NH ₃	1	1	0	1	0	0	0	0	0	-203.8	-203.8
21	ClK···NH ₃	1	1	0	0	1	0	0	0	1	-164.6	-178.8
22	Cl ₂ Be···NH ₃	1	1	0	0	0	1	0	0	0	-315.4	-315.4
23	Cl ₂ Mg···NH ₃	1	1	0	0	0	0	1	0	0	-298.0	-298.0
24	Cl ₂ Ca···NH ₃	1	1	0	0	0	0	0	1	0	-296.1	-296.1

^a Ten variables model): Base = 0 (H₂O), 1 (NH₃) Halogen = 0 (F), 1 (Cl) Metal = 1 if present, 0 absent; Li, Na, K, Be, Mg, Ca

Table S2. Comparison between the acidities and the acidity enhancements of water when attached to CO_3H_2 , SO_4H_2 and $\text{CF}_3\text{CO}_2\text{H}$ oxyacids, when calculated at the MP2/aug-cc-pVTZ and at the G4 levels of theory.

Complex	MP2/aug-cc-pVTZ		G4	
	$\Delta_{\text{acid}}\text{H}^0$	$\Delta(\Delta_{\text{acid}}\text{H}^0)$	$\Delta_{\text{acid}}\text{H}^0$	$\Delta(\Delta_{\text{acid}}\text{H}^0)$
$\text{CO}_3\text{H}_2:\text{H}_2\text{O}$	1389.3	240.5	1385.5	244.4
$\text{SO}_4\text{H}_2:\text{H}_2\text{O}$	1290.4	339.5	1294.0	335.9
$\text{CF}_3\text{CO}_2\text{H}:\text{H}_2\text{O}$	1360.5	269.4	1334.1	295.8

Table S3. Comparison between the acidities and the acidity enhancements of ammonia when attached to CO_3H_2 , SO_4H_2 and $\text{CF}_3\text{CO}_2\text{H}$ oxyacids, when calculated at the MP2/aug-cc-pVTZ and at the G4 levels of theory.

Complex	MP2/aug-cc-pVTZ		G4	
	$\Delta_{\text{acid}}\text{H}^0$	$\Delta(\Delta_{\text{acid}}\text{H}^0)$	$\Delta_{\text{acid}}\text{H}^0$	$\Delta(\Delta_{\text{acid}}\text{H}^0)$
$\text{CO}_3\text{H}_2:\text{NH}_3$	1416.1	272.7	1429.1	259.7
$\text{SO}_4\text{H}_2:\text{NH}_3$	1317.8	371.0	1342.2	346.5
$\text{CF}_3\text{CO}_2\text{H}:\text{NH}_3$	1360.5	328.8	1377.6	311.2

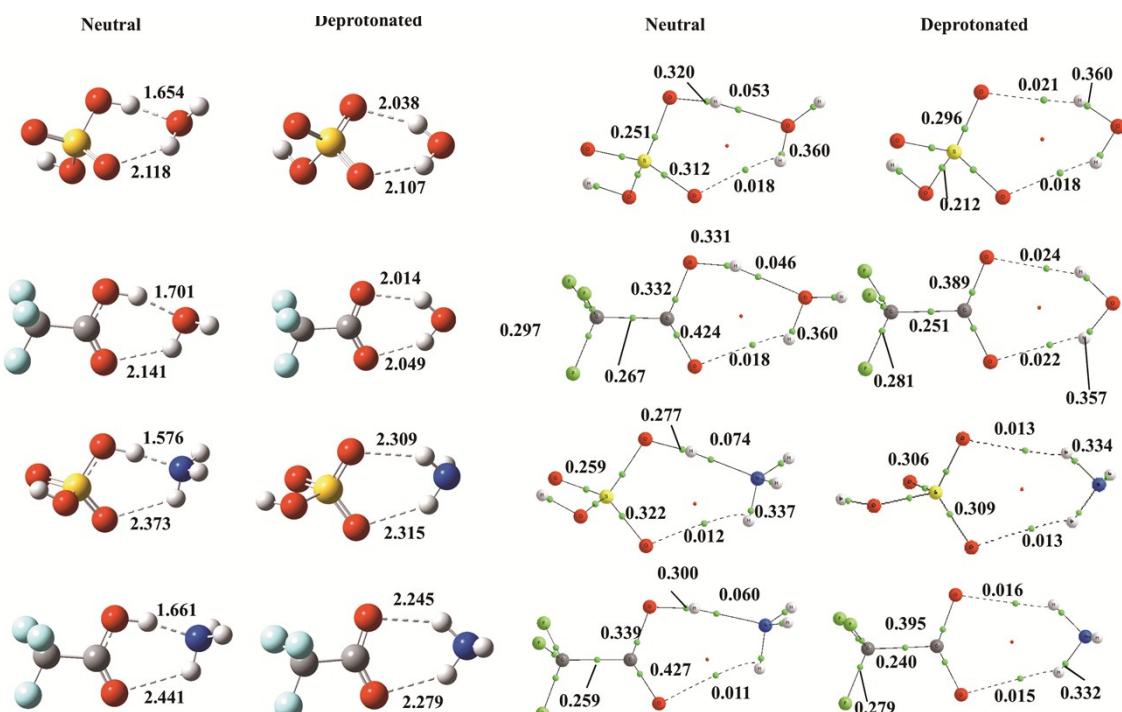


Figure S3. First two columns: MP2/aug-cc-PVTZ optimized geometries of the water and ammonia complexes with SO_4H_2 and $\text{CF}_3\text{CO}_2\text{H}$ and their corresponding deprotonated forms. Bond distances in Å. Last two columns show the corresponding molecular graphs. Green dots denote bond critical points. Electron densities are in a.u..

Table S4. Contributions to the total deformation cost on going from the neutral to the deprotonated complex (E_{def} Deprotonation). E_{def} (salt) deformation cost of the salt; E_{def}(NH₃/NH₂) deformation cost of NH₃ and NH₂⁻ for neutral complexes and deprotonated complexes, respectively. E_{def} (Complex) deformation cost of the whole complex.

Complex	E _{def} (salt)	E _{def} (NH ₃ /NH ₂)	E _{def} (Complex)	E _{def} Deprotonation ^a
SO ₄ Be_NH ₃	3.5	0.0	3.5	
SO ₄ Be_NH ₂	42.2	5.3	47.5	44.0
CO ₃ Be_NH ₃	4.9	0.0	4.9	
CO ₃ Be_NH ₂	35.6	4.8	40.4	35.5
SO ₄ Mg_NH ₃	0.0	0.0	0	
SO ₄ Mg_NH ₂	14.6	3.0	17.6	17.6
CO ₃ Mg_NH ₃	0.6	0.0	0.6	
CO ₃ Mg_NH ₂	11.3	2.8	14.2	13.6
SO ₄ Ca_NH ₃	5.1	0.0	5	
SO ₄ Ca_NH ₂	17.1	1.0	18.1	13.1
CO ₃ Ca_NH ₃	0.8	0.0	0.8	
CO ₃ Ca_NH ₂	14.4	0.9	15.3	14.5
Be Cl ₂ _NH ₃	52.2	0.0	52.2	
Be Cl ₂ _NH ₂	123.2	5.5	128.7	76.5
Mg Cl ₂ _NH ₃	15.5	0.0	15.5	
Mg Cl ₂ _NH ₂	73.3	3.2	76.5	61.0
CaCl ₂ _NH ₃	2.8	0.0	2.8	
CaCl ₂ _NH ₂	32.9	1.5	34.4	31.6

^a Energetic cost of the deformation on going from the neutral to the deprotonated complex.

Table S5. NBO Second order perturbation energies between the lone-pair of the NH₂⁻ anion and the empty orbitals of alkaline-earth derivatives in the different deprotonated complexes investigated

System		System	
SO ₄ Be_NH ₂	397	Be Cl ₂ _NH ₂	64.8
CO ₃ Be_NH ₂	389		
SO ₄ Mg_NH ₂	238	Mg Cl ₂ _NH ₂	96.9
CO ₃ Mg_NH ₂	191		
SO ₄ Ca_NH ₂	173	CaCl ₂ _NH ₂	83.7
CO ₃ Ca_NH ₂	162		