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Supplementary Information

Non-covalent Bonds in Group 1 and Group 2 Elements: The 'Alkalene bond'

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Table S1. *Correlation coefficients, intercepts and slopes of the binding energy (kJ/mol) versus electron density (au) plot for various H, Li, Na, Be, Mg and Ca bonded complexes. Values in brackets denote standard deviation.*

Complexes	CC	Intercept	Slope
X=H			
FX···A	0.92	0.3(3.0)	844(85)
HOX···A	0.94	-1.0(1.6)	832(73)
HSX···A	0.92	-0.0(1.0)	648(67)
Overall [by avg.]	0.93	-0.2(1.9)	775(75)
Overall [by fit, with (0,0)]	0.96	-2.2(0.9)	889(35)
Overall [by fit, without (0,0)]	**0.95**	**-2.5(1.0)**	**901(38)**
X=Li			
FX···A	0.86	1.0(8.7)	2868(408)
ClX···A	0.85	2.2(10.3)	2997(449)
BrX···A	0.85	2.7(10.5)	2995(450)
Overall [by avg.]	0.85	2.0(9.8)	2953(436)
Overall [by fit, with (0,0)]	0.89	0.7(4.4)	3011(199)
Overall [by fit, without (0,0)]	**0.85**	**1.1(5.4)**	**2997(239)**
X=Na			
FX···A	0.91	-12.7(6.9)	4274(484)
ClX···A	0.92	-9.9(6.4)	4039(423)
BrX···A	0.92	-9.7(6.6)	3978(428)
Overall [by avg.]	0.92	-10.8(6.6)	4097(445)
Overall [by fit, with (0,0)]	0.93	-7.0(3.0)	3840(202)
Overall [by fit, without (0,0)]	**0.91**	**-10.5(3.6)**	**4074(238)**
X=Be			
F_2X···A	0.96	-58.4(6.7)	3030(226)
Cl_2X···A	0.89	-76.7(18.2)	3090(380)
H_2X···A	0.92	-78.1(14.2)	3261(338)
Overall [by avg.]	**0.92**	**-71.1(13.0)**	**3126(315)**
Overall [by fit, with (0,0)]	**0.82**	**-38.8(9.1)**	**2408(209)**

Overall [by fit, without (0,0)]	**0.88**	**-64.9(9.1)**	**2983(206)**
X=Mg			
$F_2X\cdots A$	0.95	-20.6(7.6)	3596(277)
$Cl_2X\cdots A$	0.93	-17.7(10.0)	3569(349)
$H_2X\cdots A$	0.97	-15.3(4.2)	2960(186)
Overall [by avg.]	**0.95**	**-17.9(7.3)**	**3375(271)**
Overall [by fit, with (0,0)]	**0.93**	**-16.6(4.6)**	**3384(176)**
Overall [by fit, without (0,0)]	**0.93**	**-22.9(5.0)**	**3606(188)**
X=Ca			
$F_2X\cdots A$	0.95	-8.9(6.7)	3137(260)
$Cl_2X\cdots A$	0.94	-9.5(7.9)	3108(277)
$H_2X\cdots A$	0.95	-8.0(6.0)	2931(245)
Overall [by avg.]	**0.95**	**-8.8(6.9)**	**3059(261)**
Overall [by fit, with (0,0)]	**0.95**	**-6.6(3.2)**	**2986(125)**
Overall [by fit, without (0,0)]	**0.94**	**-9.2(3.8)**	**3081(143)**

Table S2. *Correlation coefficients (CC), intercepts and slopes of the binding energy (kJ/mol) versus electron density (au) plot for various non-covalent bonded complexes. 'Overall (by avg.)' denotes average value of correlation coefficient (CC), intercept and slope of the three sets, '**Overall [(by fit, without (0,0)]**' fits all data point without the (0,0) point]. Values in the brackets denote standard deviation. The function y=mx (without intercept) has been used to fit the data.*

Complexes	y=mx	
	CC	Slope
X=H		
FX···A	0.92	853(28)
HOX···A	0.94	788(24)
HSX···A	0.92	649(21)
Overall (by avg.)	0.93	763(24)
Overall [by fit, without (0,0)]	**0.94**	**813(19)**
X=Li		
FX···A	0.86	2914(107)
ClX···A	0.85	3088(114)
BrX···A	0.85	3107(114)
Overall (by avg.)	0.85	3036(112)
Overall [by fit, without (0,0)]	**0.85**	**3042(64)**
X=Na		
FX···A	0.87	3411(137)
ClX···A	0.90	3408(113)
BrX···A	0.89	3372(112)
Overall (by avg.)	0.89	3397(121)
Overall [by fit, without (0,0)]	**0.89**	**3396(67)**

X=Be		
$F_2X\cdots A$	0.76	1700(119)
$Cl_2X\cdots A$	0.65	1524(134)
$H_2X\cdots A$	0.62	1441(139)
Overall (by avg.)	0.68	1555(131)
Overall [by fit, without (0,0)]	**0.67**	**1554(75)**
X=Mg		
$F_2X\cdots A$	0.91	2875(96)
$Cl_2X\cdots A$	0.90	2976(103)
$H_2X\cdots A$	0.94	2316(94)
Overall (by avg.)	0.92	2722(98)
Overall [by fit, without (0,0)]	**0.88**	**2779(74)**
X=Ca		
$F_2X\cdots A$	0.94	2803(77)
$Cl_2X\cdots A$	0.93	2789(76)
$H_2X\cdots A$	0.94	2623(79)
Overall(by avg)	0.94	2738(77)
Overall [by fit, without (0,0)]	**0.93**	**2745(45)**

Table S3*. Power fit ($y=ax^r$) of the binding energy (kJ/mol) versus electron density (au) data for various non-covalent bonded complexes formed by different elements. The values of the pre factor, a, and the power, r, and standard deviation from the fit, are given. Columns 1 and 2 include the correlation coefficients (CC) from the linear and power fits, which may be used to compare the fit. For Be bond, the power (r) is close to or greater than 2.00 (in bold).*

Elements	Linear Fit CC	Power fit CC	a	r
H	0.95	0.95	1248(220)	1.12(0.05)
Li	0.85	0.85	2585(894)	0.96(0.09)
Na	0.91	0.91	8854(3429)	1.23(0.09)
Be	**0.88**	**0.92**	**61627(30220)**	**2.21(0.16)**
Mg	0.93	0.93	11780(3628)	1.41(0.09)
Ca	0.94	0.94	4428(982)	1.13(0.06)

Table S4: *Correlation coefficients (CC), intercept, and slope for group 1 and group 2 elements with and without correcting the Basis Set Superposition Error (BSSE) in energy.*

Elements	With BSSE Corrected Energy			Without BSSE Corrected Energy		
	CC	Intercept	Slope	CC	Intercept	Slope
H	0.95	-2.5(1.0)	901(38)	0.97	-0.12(0.89)	986(35)
Li	0.85	1.1(5.4)	2997(239)	0.86	4.9(5.4)	3176(238)
Na	0.91	-10.5(3.6)	4074(238)	0.94	-9.1(3.2)	4256(210)
Be	0.88	-64.9(9.1)	2983(206)	0.88	-62.7(9.6)	3164(217)
Mg	0.93	-22.9(5.0)	3606(188)	0.92	-20.2(5.3)	3713(201)
Ca	0.94	-9.2(3.8)	3081(143)	0.94	-7.4(4.2)	3260(160)

Table S5: *Comparison of slope from other studies and present work. References are from main text.*

Method	CC	Intercept	Slope	Reference
		H		
MP2(full)/aug-cc-pVTZ	0.88	-0.4	777	[37]
MP2(full)/aug-cc-pVTZ	0.98	-5.1	1101	[83]
B3LYP/6-311++G(d,p)	0.86	-2.9(5.6)	911(141)	[97]
MP2/aug-cc-pVDZ	**0.95**	**-2.5(1.0)**	**901(38)**	This work
		Li		
MP2(full)/aug-cc-pVTZ	0.97	-17.6	3271	[37]
MP2(full)/aug-cc-pVTZ	0.96	-13.1	3218	[83]
MP2/aug-cc-pVDZ	**0.85**	**1.1(5.4)**	**2997(239)**	This work
		Na		
MP2(full)/6-311++G(d,p)	0.90	18.0(9.6)	4699(536)	[34]
MP2/aug-cc-pVDZ	**0.91**	**-10.5(3.6)**	**4074(238)**	This work
		Be		
CCSD(T)/aug-cc-pVTZ	0.87	-64.1(16.6)	2600(308)	[40]
G4	0.77	-68.0(46.3)	2813(694)	[44]
MP2/aug-cc-pVDZ	**0.88**	**-64.9(9.1)**	**2983(206)**	This work
		Mg		
B3LYP/6-311+G(3df,2p)	0.93	-29.2(13.7)	3599(466)	[46]
MP2/aug-cc-pVDZ	**0.93**	**-22.9(5.0)**	**3606(188)**	This work
		Ca		
G4	0.97	-3.0(18.6)	3082(566)	[49]
MP2/aug-cc-pVDZ	**0.94**	**-9.2(3.8)**	**3081(143)**	This work

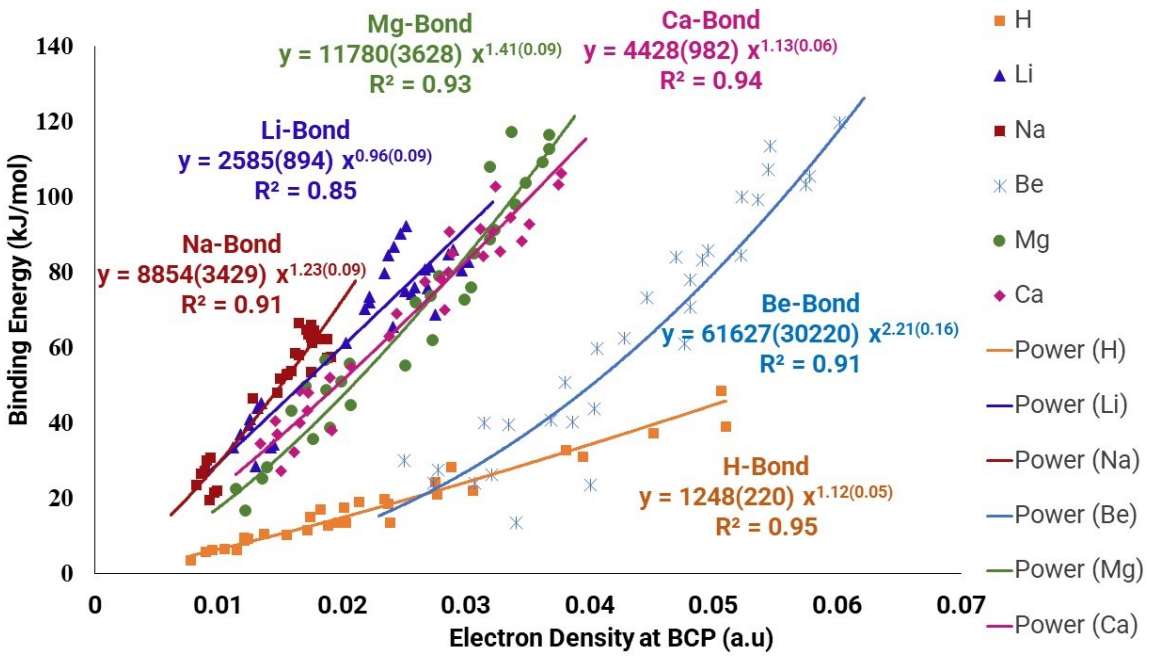

Figure S1. *Power fit (ax^r) of the binding energy (kJ/mol) versus electron density (au) for alkalene (Li, Na, Be, Mg, Ca) and hydrogen (H) bonded complexes. Values of the prefactor (a) and power (r) of the best fit lines are shown along with their respective standard deviation. The R^2 value denotes the quality of the fit.*

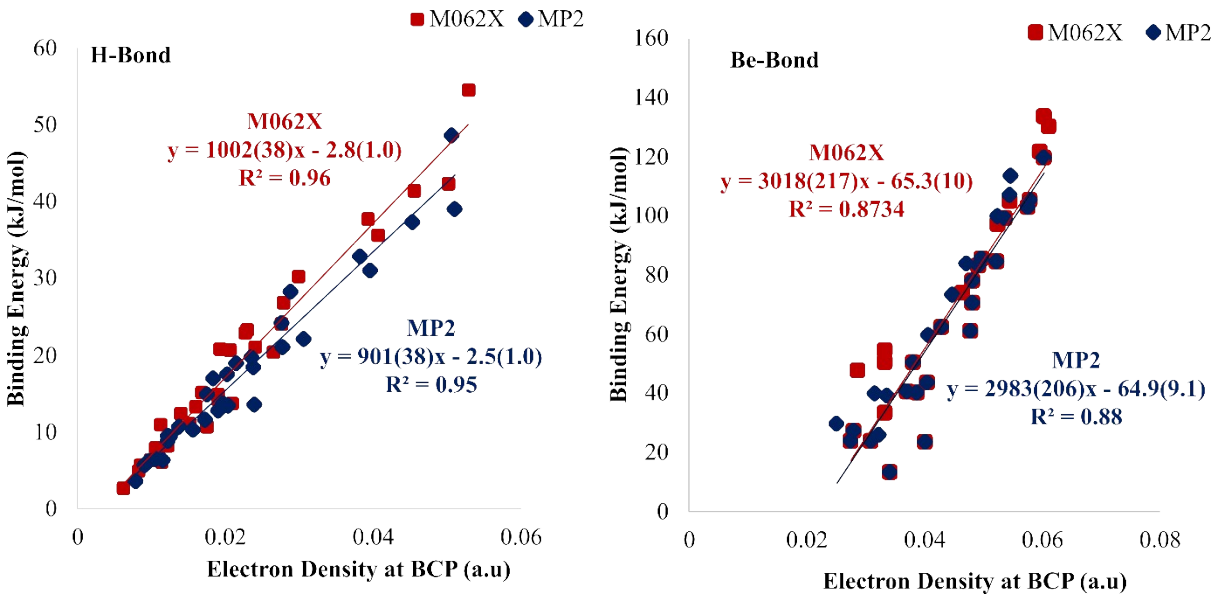

Figure S2*. Comparison of slopes and intercepts from binding energy and electron density plots obtained from M062X and MP2 methods for H and Be-bonds.*

The following section contains all data sets. (Tables D1 to D6 and Figures D1 to D6).

All Data Sets

Table D1. *Electron density at BCP (au) and binding energy (kJ/mol) data for H-bonded complexes.*

Complexes	Electron Density (au)	Binding Energy (kJ/mol)
$FH\bullet\bullet\bullet OH_2$	0.0381	32.9
$FH\bullet\bullet\bullet SH_2$	0.0214	19.0
$FH\bullet\bullet\bullet NH_3$	0.0506	48.7
$FH\bullet\bullet\bullet NCH$	0.0288	28.3
$FH\bullet\bullet\bullet CO$	0.0203	13.5
$FH\bullet\bullet\bullet HCHO$	0.0395	31.1
$FH\bullet\bullet\bullet C_2H_4$	0.0183	17.1
$FH\bullet\bullet\bullet CH_3OH$	0.0452	37.4
$FH\bullet\bullet\bullet PH_3$	0.0202	17.6
$FH\bullet\bullet\bullet O(CH_3)_2$	0.051	39.1
$HOH\bullet\bullet\bullet OH_2$	0.0237	18.5
$HOH\bullet\bullet\bullet SH_2$	0.0137	10.7
$HOH\bullet\bullet\bullet NH_3$	0.0275	24.3
$HOH\bullet\bullet\bullet NCH$	0.0174	15.0
$HOH\bullet\bullet\bullet CO$	0.0115	6.4
$HOH\bullet\bullet\bullet OCH_2$	0.0234	19.8
$HOH\bullet\bullet\bullet C_2H_4$	0.0121	9.5
$HOH\bullet\bullet\bullet OHCH_3$	0.0277	21.1
$HOH\bullet\bullet\bullet PH_3$	0.0121	8.9
$HOH\bullet\bullet\bullet O(CH_3)_2$	0.0306	22.1
$HSH\bullet\bullet\bullet OH_2$	0.0155	10.4
$HSH\bullet\bullet\bullet SH_2$	0.0105	6.5
$HSH\bullet\bullet\bullet NH_3$	0.0197	13.7
$HSH\bullet\bullet\bullet NCH$	0.0124	9.4
$HSH\bullet\bullet\bullet CO$	0.0078	3.6
$HSH\bullet\bullet\bullet OCH_2$	0.0172	11.7
$HSH\bullet\bullet\bullet C_2H_4$	0.0095	6.3
$HSH\bullet\bullet\bullet OHCH_3$	0.0189	12.9
$HSH\bullet\bullet\bullet PH_3$	0.009	5.7
$HSH\bullet\bullet\bullet O(CH_3)_2$	0.0239	13.6

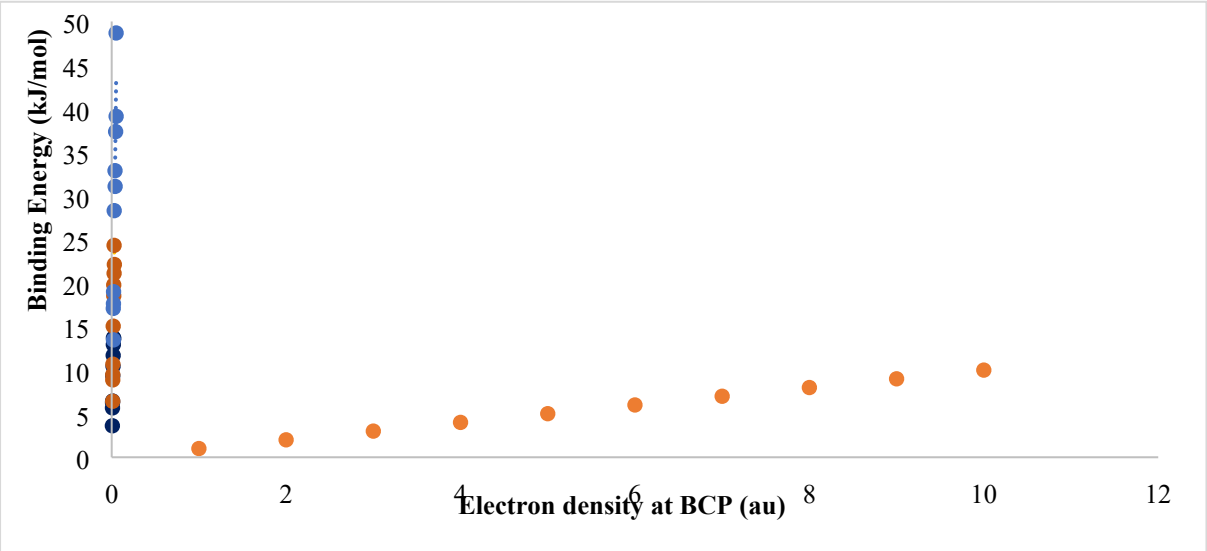

Figure D1*. Binding energy (kJ/mol) versus electron density at BCP (au) plot for H-bonded complexes*

Table D2. *Electron density at BCP (au) and binding energy (kJ/mol) data for Li-bonded complexes.*

Complexes	Electron Density (au)	Binding Energy (kJ/mol)
$FLi\cdots OH_2$	0.0241	65.7
$FLi\cdots NCCH_3$	0.0222	73.7
$FLi\cdots NH_3$	0.0234	79.9
FLi•••NCH	0.0203	61.3
$FLi\cdots OCH_2$	0.0251	75.0
$FLi\cdots C_2H_4$	0.0112	33.5
$FLi\cdots OHCH_3$	0.0269	75.9
$FLi\cdots PH_3$	0.0118	37.0
FLi•••CO	0.013	28.7
$FLi\cdots O(CH_3)_2$	0.0275	68.8
$ClLi\cdots OH_2$	0.0256	74.3
$ClLi\cdots NCCH_3$	0.0237	84.5
$ClLi\cdots NH_3$	0.0247	90.3
ClLi•••NCH	0.0218	70.3
$ClLi\cdots OCH_2$	0.0267	80.9
$ClLi\cdots C_2H_4$	0.0125	39.7
$ClLi\cdots OHCH_3$	0.0286	84.8
$ClLi\cdots PH_3$	0.0132	44.0
ClLi•••CO	0.0142	33.5
$ClLi\cdots O(CH_3)_2$	0.0297	80.7
$BrLi\cdots OH_2$	0.0259	76.2
$BrLi\cdots NCCH_3$	0.0242	86.8
$BrLi\cdots NH_3$	0.0252	92.4
BrL•••NCH	0.0222	72.2
$BrLi\cdots OCH_2$	0.0271	81.7
$BrLi\cdots C_2H_4$	0.0126	41.0
$BrLi\cdots OHCH_3$	0.029	86.3
$BrLi\cdots PH_3$	0.0135	45.4
BrLi•••CO	0.0145	34.4
$BrLi\cdots O(CH_3)_2$	0.0302	82.7

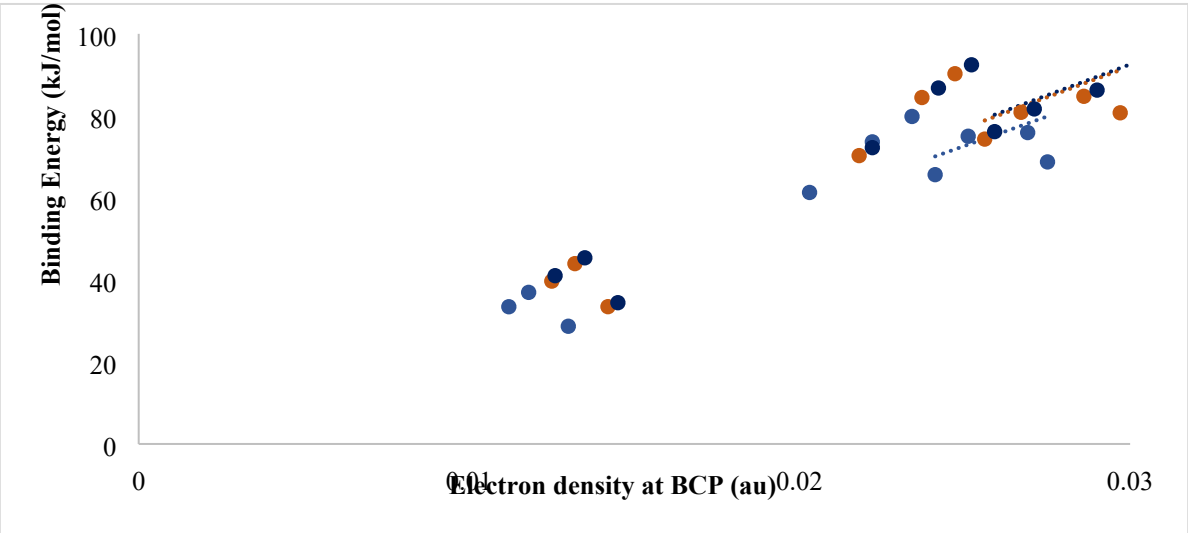

Figure D2*. Binding energy (kJ/mol) versus electron density at BCP (au) plot for Li- bonded complexes.*

Table D3. *Electron density at BCP (au) and binding energy (kJ/mol) data for Na-bonded complexes.*

Complexes	Electron Density (au)	Binding Energy (kJ/mol)
$FNa\cdots OH_2$	0.0128	46.5
$FNa\cdots NCCH_3$	0.0162	58.7
$FNa\cdots NH_3$	0.0165	58.0
FNa•••NCH	0.0148	48.0
$FNa\cdots OCH_2$	0.0165	66.5
$FNa\cdots C_2H_4$	0.0082	23.5
$FNa\cdots OHCH_3$	0.0176	61.4
$FNa\cdots PH_3$	0.0086	26.7
FNa•••CO	0.0093	19.6
$FNa\cdots O(CH_3)_2$	0.0175	53.7
$ClNa\cdots OH_2$	0.015	51.9
$ClNa\cdots NCCH_3$	0.0171	64.8
$ClNa\cdots NH_3$	0.0174	63.6
ClNa•••NCH	0.0156	53.0
$ClNa\cdots OCH_2$	0.0173	63.6
$ClNa\cdots C_2H_4$	0.0087	26.7
$ClNa\cdots OHCH_3$	0.0184	62.4
$ClNa\cdots PH_3$	0.0091	30.1
ClNa•••CO	0.0097	21.7
$ClNa\cdots O(CH_3)_2$	0.0188	57.4
$BrNa\cdots OH_2$	0.0155	52.9
$BrNa\cdots NCCH_3$	0.0175	66.1
$BrNa\cdots NH_3$	0.0177	64.7
BrNa•••NCH	0.0159	53.9
BrNa••• OCH_2	0.0175	62.8
$BrNa\cdots C_2H_4$	0.0089	27.3
$BrNa\cdots OHCH_3$	0.0188	62.3
$BrNa\cdots PH_3$	0.0094	30.8
BrNa•••CO	0.0099	22.1
$BrNa\cdots O(CH_3)_2$	0.0191	57.7

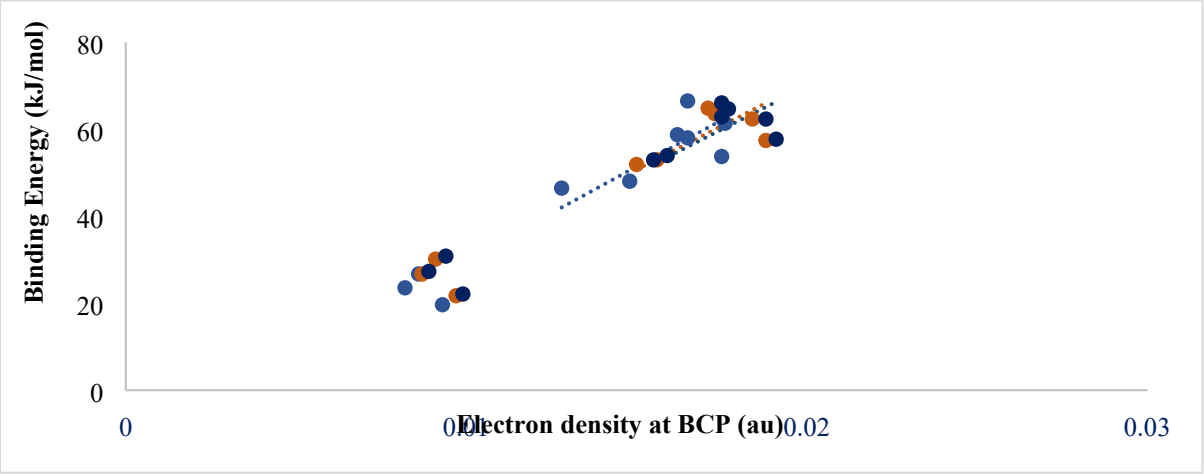

Figure D3. *Binding energy (kJ/mol) versus electron density at BCP (au) plot for Na-bonded complexes.*

Table D4. *Electron density at BCP (au) and binding energy (kJ/mol) data for Be-bonded complexes.*

Complexes	Electron Density (au)	Binding Energy (kJ/mol)
$F_2Be{\bullet\bullet\bullet}OH_2$	0.047	84.0
$F_2Be{\bullet\bullet\bullet}SH_2$	0.0315	40.0
$F_2Be{\bullet\bullet\bullet}NH_3$	0.0546	113.7
$F_2Be{\bullet\bullet\bullet}NCH$	0.0406	59.8
$F_2Be{\bullet\bullet\bullet}OCH_2$	0.0446	73.4
$F_2Be{\bullet\bullet\bullet}C_2H_4$	0.025	30.0
$F_2Be{\bullet\bullet\bullet}OHCH_3$	0.0523	100.0
$F_2Be{\bullet\bullet\bullet}PH_3$	0.0335	39.6
$F_2Be{\bullet\bullet\bullet}CO$	0.0321	26.3
$F_2Be{\bullet\bullet\bullet}O(CH_3)_2$	0.0544	107.3
$Cl_2Be{\bullet\bullet\bullet}OH_2$	0.0522	84.7
$Cl_2Be{\bullet\bullet\bullet}SH_2$	0.0369	40.8
$Cl_2Be{\bullet\bullet\bullet}NH_3$	0.0602	119.8
$Cl_2Be{\bullet\bullet\bullet}NCH$	0.0477	61.2
$Cl_2Be{\bullet\bullet\bullet}OCH_2$	0.0481	70.8
$Cl_2Be{\bullet\bullet\bullet}C_2H_4$	0.0278	27.6
$Cl_2Be{\bullet\bullet\bullet}OHCH_3$	0.0575	103.3
$Cl_2Be{\bullet\bullet\bullet}PH_3$	0.0404	43.8
$Cl_2Be{\bullet\bullet\bullet}CO$	0.0401	23.6
$Cl_2Be{\bullet\bullet\bullet}O(CH_3)_2$	0.0578	105.7
$H_2Be{\bullet\bullet\bullet}OH_2$	0.0428	62.7
$H_2Be{\bullet\bullet\bullet}SH_2$	0.0274	24.2
$H_2Be{\bullet\bullet\bullet}NH_3$	0.0496	85.9
$H_2Be{\bullet\bullet\bullet}NCH$	0.0386	40.3
$H_2Be{\bullet\bullet\bullet}OCH_2$	0.038	50.8
$H_2Be{\bullet\bullet\bullet}NH_2CH_3$	0.0536	99.3
$H_2Be{\bullet\bullet\bullet}OHCH_3$	0.0481	78.2
$H_2Be{\bullet\bullet\bullet}PH_3$	0.0307	24.1
$H_2Be{\bullet\bullet\bullet}CO$	0.0341	13.7
$H_2Be{\bullet\bullet\bullet}O(CH_3)_2$	0.0491	83.3

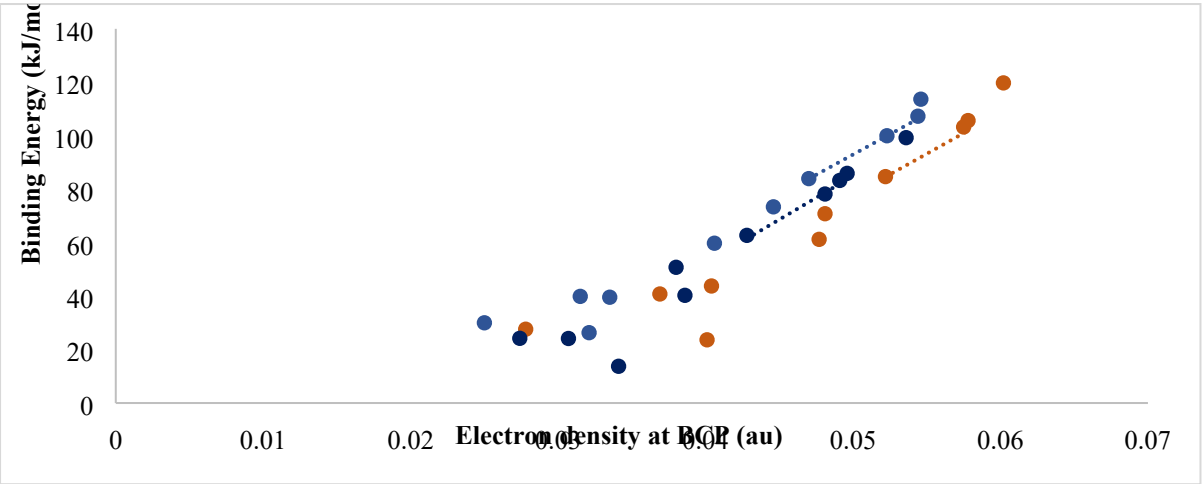

Figure D4*. Binding energy (kJ/mol) versus electron density at BCP (au) plot for Be-bonded complexes.*

Table D5. *Electron density at BCP (au) and binding energy (kJ/mol) data for Mg-bonded complexes.*

Complexes	Electron Density (au)	Binding Energy (kJ/mol)
$F_2Mg\cdots OH_2$	0.0324	91.0
$F_2Mg\cdots SH_2$	0.02	50.9
$F_2Mg\cdots NH_3$	0.032	107.9
$F_2Mg\cdots NCH$	0.026	71.9
$F_2Mg\cdots OCH_2$	0.0307	84.8
$F_2Mg\cdots C_2H_4$	0.016	43.1
$F_2Mg\cdots OHCH_3$	0.0349	103.7
$F_2Mg\cdots PH_3$	0.0188	48.5
$F_2Mg\cdots CO$	0.0177	35.5
$F_2Mg\cdots O(CH_3)_2$	0.0363	109.2
$Cl_2Mg\cdots OH_2$	0.0341	97.8
$Cl_2Mg\cdots SH_2$	0.0187	56.7
$Cl_2Mg\cdots NH_3$	0.0338	117.2
$Cl_2Mg\cdots NCH$	0.0279	78.9
$Cl_2Mg\cdots HCHO$	0.032	88.5
$Cl_2Mg\cdots C_2H_4$	0.0171	49.6
$Cl_2Mg\cdots OHCH_3$	0.0368	112.7
$Cl_2Mg\cdots PH_3$	0.0207	55.7
$Cl_2Mg\cdots CO$	0.0191	38.5
$Cl_2Mg\cdots O(CH_3)_2$	0.0368	116.4
$H_2Mg\cdots OH_2$	0.0274	61.9
$H_2Mg\cdots SH_2$	0.014	28.2
$H_2Mg\cdots NH_3$	0.0272	73.7
$H_2Mg\cdots NCH$	0.0208	44.5
$H_2Mg\cdots OCH_2$	0.0252	55.0
$H_2Mg\cdots C_2H_4$	0.0115	22.4
$H_2Mg\cdots OHCH_3$	0.03	72.6
$H_2Mg\cdots PH_3$	0.0136	25.2
$H_2Mg\cdots CO$	0.0123	16.5
$H_2Mg\cdots O(CH_3)_2$	0.0305	75.9

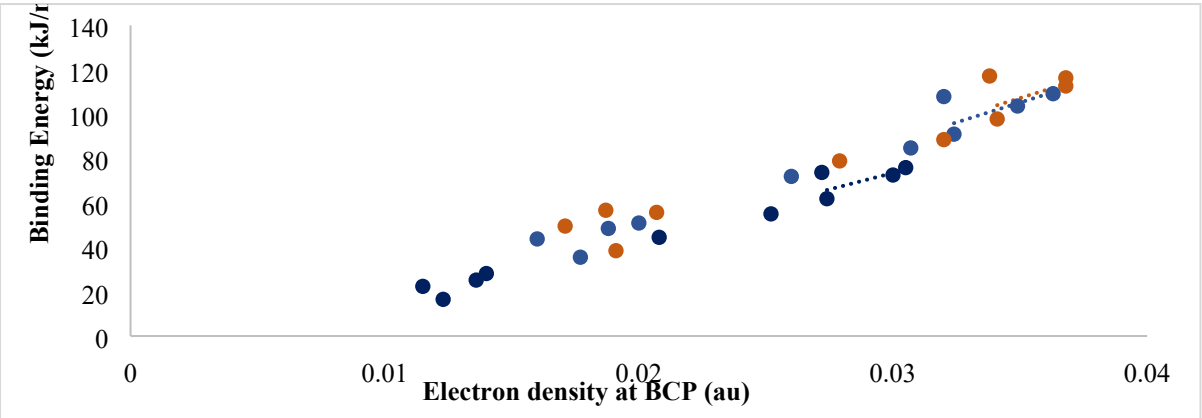

Figure D5. *Binding energy (kJ/mol) versus electron density at BCP (au) plot for Mg- bonded complexes.*

Table D6. *Electron density at BCP (au) and binding energy (kJ/mol) data for Ca-bonded complexes.*

Complexes	Electron Density (au)	Binding Energy (kJ/mol)
$F_2Ca\cdots OH_2$	0.0312	91.7
$F_2Ca\cdots SH_2$	0.0173	48.0
$F_2Ca\cdots NH_3$	0.0287	90.9
$F_2Ca\cdots NCH$	0.0244	69.1
$F_2Ca\cdots CO$	0.0161	32.4
$F_2Ca\cdots OCH_2$	0.0286	80.0
$F_2Ca\cdots C_2H_4$	0.0146	40.6
$F_2Ca\cdots OHCH_3$	0.032	91.3
$F_2Ca\cdots PH_3$	0.0172	43.4
$F_2Ca\cdots O(CH_3)_2$	0.0351	92.9
$Cl_2Ca\cdots OH_2$	0.0336	94.5
$Cl_2Ca\cdots SH_2$	0.0208	54.8
$Cl_2Ca\cdots NH_3$	0.0324	102.9
$Cl_2Ca\cdots NCH$	0.028	78.3
$Cl_2Ca\cdots CO$	0.0192	38.2
$Cl_2Ca\cdots OCH_2$	0.0314	84.4
$Cl_2Ca\cdots C_2H_4$	0.0166	48.6
$Cl_2Ca\cdots OHCH_3$	0.0375	103.3
$Cl_2Ca\cdots PH_3$	0.019	52.0
$Cl_2Ca\cdots O(CH_3)_2$	0.0377	106.4
$H_2Ca\cdots SH_2$	0.0166	40.0
$H_2Ca\cdots NH_3$	0.0289	85.0
$H_2Ca\cdots NCH$	0.0238	63.0
$H_2Ca\cdots CO$	0.0151	27.3
$H_2Ca\cdots OCH_2$	0.0283	70.1
$H_2Ca\cdots C_2H_4$	0.0134	34.6
$H_2Ca\cdots OHCH_3$	0.0328	85.6
$H_2Ca\cdots PH_3$	0.0148	37.1
$H_2Ca\cdots O(CH_3)_2$	0.0345	88.3
$H_2Ca\cdots CH_3CN$	0.0267	77.6

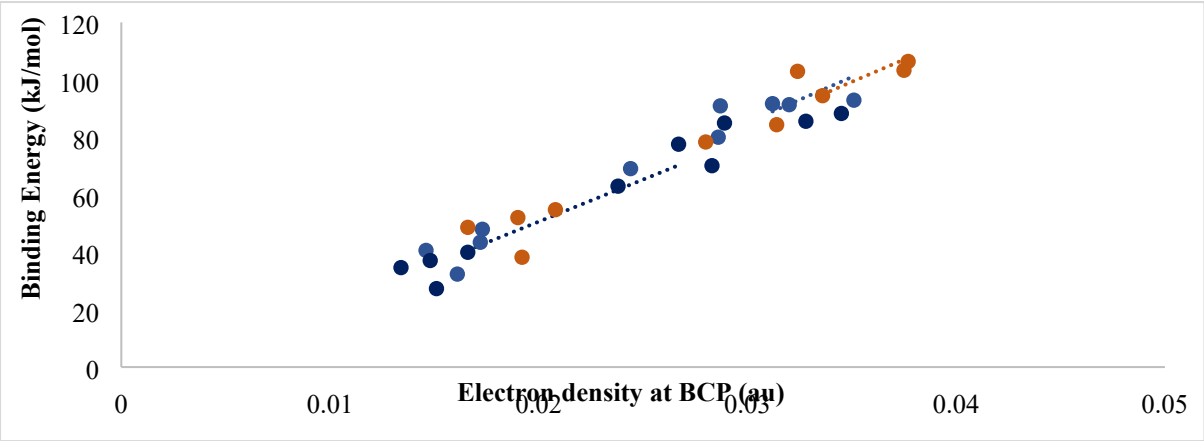

Figure D6. *Binding energy (kJ/mol) versus electron density at BCP (au) plot for Ca- bonded complexes.*