Journal of the Serbian Chemical Society

*J. Serb. Chem. Soc. 82* (10) S404–S412 (2017) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

# Structural and electronic effects of cation binding ($Li^+$, $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$) to the π system of the $\eta^6$-benzene–$Cr(CO)_3$ complex: a theoretical study

AYYAVOO KALPANA and LAKSHMINARAYANAN AKILANDESWARI*

*Department of Chemistry, Sri Sarada College for Women, Salem 636 016, TamilNadu, India*

*J. Serb. Chem. Soc. 82* (10) (2017) 1123–1134

TABLE S-I. Computed $\lambda_{max}$ (maximum absorption wavelength), nm, *f* (oscillator strength), *TDM* (transition dipole moments), root mean square value, *RMS*, e-bohr, between the ground and $n^{th}$ excited state of all the systems under study; Data corresponding to the maximum absorption wavelength are in bold letters

| System | MB | | | | | | |
|---|---|---|---|---|---|---|---|
| | State transition | λ / nm | *f* | Transition dipole moment | | | *RMS* |
| | | | | *x* | *y* | *z* | e-bohr |
| BC | $S_0 \rightarrow S_3$ | 168.03 | 0.5587 | –0.1278 | –0.4628 | 0.0000 | 0.480 |
| | **$S_0 \rightarrow S_4$** | **168.03** | **0.5588** | **–0.4629** | **0.1278** | **0.0000** | **0.480** |
| | $S_0 \rightarrow S_8$ | 155.08 | 0.0056 | 0.0000 | 0.0000 | –0.0087 | 0.009 |
| $Li^+$–BC | $S_0 \rightarrow S_2$ | 193.20 | 0.0202 | 0.0085 | 0.0635 | 0.0000 | 0.064 |
| | $S_0 \rightarrow S_3$ | 193.19 | 0.0202 | –0.0636 | 0.0084 | 0.0000 | 0.064 |
| | **$S_0 \rightarrow S_6$** | **165.65** | **0.5223** | **–0.1315** | **0.4292** | **0.0000** | **0.449** |
| | $S_0 \rightarrow S_7$ | 165.65 | 0.5222 | –0.4292 | –0.1315 | 0.0000 | 0.449 |
| | $S_0 \rightarrow S_{10}$ | 163.62 | 0.0066 | 0.0000 | 0.0001 | –0.0277 | 0.028 |
| $Na^+$–BC | $S_0 \rightarrow S_1$ | 230.59 | 0.0111 | –0.0067 | 0.0494 | 0.0001 | 0.050 |
| | $S_0 \rightarrow S_2$ | 230.57 | 0.0111 | 0.0495 | 0.0069 | 0.0001 | 0.050 |
| | **$S_0 \rightarrow S_5$** | **168.36** | **0.5276** | **–0.0938** | **0.444** | **0.0009** | **0.454** |
| | $S_0 \rightarrow S_6$ | 168.35 | 0.5276 | 0.4441 | 0.0938 | 0.001 | 0.454 |
| $K^+$–BC | $S_0 \rightarrow S_1$ | 230.94 | 0.0085 | 0.0000 | 0.0002 | –0.0395 | 0.040 |
| | $S_0 \rightarrow S_2$ | 230.93 | 0.0085 | 0.0000 | –0.0395 | –0.0002 | 0.040 |
| | $S_0 \rightarrow S_5$ | 172.58 | 0.0001 | –0.0055 | 0.0000 | 0.0001 | 0.006 |
| | $S_0 \rightarrow S_7$ | 171.21 | 0.1136 | 0.1767 | –0.0001 | 0.0000 | 0.177 |
| | $S_0 \rightarrow S_9$ | 169.78 | 0.3383 | 0.0000 | –0.2698 | 0.2307 | 0.355 |
| | **$S_0 \rightarrow S_{10}$** | **169.76** | **0.3436** | **–0.0001** | **0.233** | **0.2718** | **0.358** |
| $Mg^{2+}$–BC | $S_0 \rightarrow S_1$ | 334.30 | 0.0014 | 0.0098 | 0.0108 | 0/0000 | 0.015 |
| | $S_0 \rightarrow S_2$ | 334.28 | 0.0014 | –0.0107 | 0.0098 | –0.0001 | 0.015 |
| | **$S_0 \rightarrow S_8$** | **174.03** | **0.0109** | **0.0000** | **0.0000** | **–0.0519** | **0.052** |

* Corresponding author. E-mail: akilchem@gmail.com

TABLE S-I. Continued

| System | State transition | $\lambda$ / nm | $f$ | Transition dipole moment | | | *RMS* e-bohr |
|---|---|---|---|---|---|---|---|
| | | | | *x* | *y* | *z* | |
| | | | MB | | | | |
| $Ca^{2+}$–BC | $S_0 \rightarrow S_1$ | 296.74 | 0.0027 | 0.0000 | 0.0000 | 0.0157 | 0.016 |
| | $S_0 \rightarrow S_2$ | 296.72 | 0.0027 | 0.0000 | 0.0157 | 0.0000 | 0.016 |
| | **$S_0 \rightarrow S_{10}$** | **173.55** | **0.0069** | **0.0335** | **–0.0001** | **0.0000** | **0.034** |
| | | | MBC | | | | |
| BC | $S_0 \rightarrow S_2$ | 361.16 | 0.0004 | –0.0011 | –0.0122 | 0.0661 | 0.067 |
| | $S_0 \rightarrow S_3$ | 361.10 | 0.0004 | –0.0006 | 0.0657 | 0.0121 | 0.067 |
| | $S_0 \rightarrow S_4$ | 346.01 | 0.0002 | 0.0323 | 0.0405 | –0.0043 | 0.052 |
| | $S_0 \rightarrow S_5$ | 345.91 | 0.0010 | –0.0093 | 0.0202 | –0.1022 | 0.105 |
| | $S_0 \rightarrow S_6$ | 345.80 | 0.0009 | –0.0117 | 0.0954 | 0.0238 | 0.099 |
| | $S_0 \rightarrow S_7$ | 344.98 | 0.0005 | 0.0720 | 0.0005 | –0.0060 | 0.072 |
| | **$S_0 \rightarrow S_8$** | **328.93** | **0.0016** | **–0.0002** | **–0.1242** | **–0.0418** | **0.131** |
| | $S_0 \rightarrow S_9$ | 328.89 | 0.0016 | 0.0008 | –0.0419 | 0.1247 | 0.132 |
| | $S_0 \rightarrow S_{10}$ | 308.11 | 0.0001 | 0.0006 | –0.0353 | –0.0010 | 0.035 |
| $Li^+$–BC | $S_0 \rightarrow S_4$ | 390.76 | 0.0006 | –0.0051 | –0.0323 | 0.0820 | 0.088 |
| | $S_0 \rightarrow S_5$ | 390.42 | 0.0006 | 0.0013 | –0.0824 | –0.0336 | 0.089 |
| | **$S_0 \rightarrow S_6$** | **352.21** | **0.0025** | **0.1700** | **0.0058** | **0.0026** | **0.170** |
| | $S_0 \rightarrow S_7$ | 349.04 | 0.0013 | 0.0925 | –0.0814 | 0.0041 | 0.123 |
| | $S_0 \rightarrow S_8$ | 348.72 | 0.0012 | –0.0476 | –0.0692 | –0.0820 | 0.117 |
| | $S_0 \rightarrow S_9$ | 348.49 | 0.0013 | 0.0531 | 0.0593 | –0.0911 | 0.121 |
| | $S_0 \rightarrow S_{10}$ | 322.44 | 0.0006 | 0.0060 | 0.0061 | –0.0785 | 0.079 |
| $Na^+$–BC | $S_0 \rightarrow S_2$ | 398.04 | 0.0006 | 0.0000 | –0.0337 | 0.0837 | 0.090 |
| | $S_0 \rightarrow S_3$ | 397.86 | 0.0006 | 0.0018 | 0.0831 | 0.0338 | 0.090 |
| | $S_0 \rightarrow S_4$ | 391.39 | 0.0001 | –0.0007 | –0.0035 | 0.0404 | 0.041 |
| | $S_0 \rightarrow S_5$ | 391.27 | 0.0001 | 0.0007 | 0.0414 | 0.0036 | 0.042 |
| | $S_0 \rightarrow S_8$ | 367.94 | 0.0012 | –0.1217 | –0.0008 | –0.0002 | 0.122 |
| | **$S_0 \rightarrow S_9$** | **351.84** | **0.0015** | **0.0012** | **–0.1334** | **0.0118** | **0.134** |
| | $S_0 \rightarrow S_{10}$ | 351.64 | 0.0015 | 0.0001 | –0.0119 | –0.1333 | 0.134 |
| $K^+$–BC | $S_0 \rightarrow S_4$ | 379.73 | 0.0007 | 0.0019 | 0.0929 | 0.0145 | 0.094 |
| | $S_0 \rightarrow S_5$ | 379.42 | 0.0007 | –0.0026 | –0.0143 | 0.0924 | 0.094 |
| | $S_0 \rightarrow S_6$ | 377.77 | 0.0001 | –0.0001 | 0.0292 | –0.0173 | 0.034 |
| | $S_0 \rightarrow S_7$ | 377.69 | 0.0001 | –0.0002 | –0.0152 | –0.0304 | 0.034 |
| | $S_0 \rightarrow S_9$ | 341.11 | 0.0001 | –0.0332 | –0.0051 | –0.0049 | 0.034 |
| | **$S_0 \rightarrow S_{10}$** | **339.76** | **0.0013** | **–0.0026** | **–0.0183** | **0.1175** | **0.119** |
| $Mg^{2+}$–BC | $S_0 \rightarrow S_1$ | 1096.59 | 0.0002 | 0.0018 | 0.0651 | 0.0407 | 0.077 |
| | $S_0 \rightarrow S_2$ | 1095.48 | 0.0002 | 0.0018 | 0.0401 | –0.0655 | 0.077 |
| | **$S_0 \rightarrow S_3$** | **792.33** | **0.0484** | **–1.1238** | **–0.0011** | **0.0001** | **1.124** |
| | $S_0 \rightarrow S_5$ | 402.55 | 0.0001 | 0.0020 | –0.0285 | –0.0024 | 0.029 |
| | $S_0 \rightarrow S_6$ | 402.43 | 0.0001 | –0.0014 | 0.0018 | –0.0282 | 0.028 |
| | $S_0 \rightarrow S_7$ | 395.43 | 0.0001 | –0.0007 | 0.0356 | 0.0053 | 0.036 |
| | $S_0 \rightarrow S_8$ | 395.14 | 0.0001 | 0.0001 | –0.0057 | 0.0363 | 0.037 |
| | $S_0 \rightarrow S_9$ | 374.08 | 0.0016 | 0.0000 | 0.1391 | –0.0113 | 0.140 |
| | $S_0 \rightarrow S_{10}$ | 373.93 | 0.0016 | 0.0010 | 0.0112 | 0.1395 | 0.140 |

TABLE S-I. Continued

| System | MB | | | | | | |
|---|---|---|---|---|---|---|---|
| | State transition | $\lambda$ / nm | $f$ | Transition dipole moment | | | *RMS* e-bohr |
| | | | | $x$ | $y$ | $z$ | |
| | | | MBC | | | | |
| $Ca^{2+}$–BC | $S_0 \rightarrow S_1$ | 744.07 | 0.0003 | 0.0002 | 0.0394 | –0.0834 | 0.092 |
| | $S_0 \rightarrow S_2$ | 743.49 | 0.0003 | 0.0013 | 0.0835 | 0.0395 | 0.092 |
| | **$S_0 \rightarrow S_3$** | **667.06** | **0.0174** | **–0.6181** | **0.0001** | **–0.0001** | **0.618** |
| | $S_0 \rightarrow S_5$ | 430.26 | 0.0001 | 0.0008 | –0.0075 | –0.0359 | 0.037 |
| | $S_0 \rightarrow S_6$ | 430.18 | 0.0001 | –0.0001 | 0.0359 | –0.0077 | 0.037 |
| | $S_0 \rightarrow S_9$ | 374.44 | 0.0009 | 0.0003 | –0.0892 | 0.0523 | 0.103 |
| | $S_0 \rightarrow S_{10}$ | 374.36 | 0.0009 | 0.0003 | –0.0518 | –0.0892 | 0.103 |

TABLE S-II. NTO pictures and MO transitions corresponding to $\lambda_{max}$ / nm of the MB systems under study

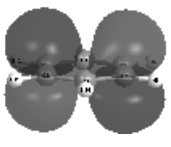
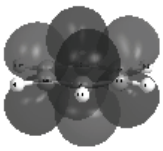
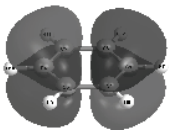
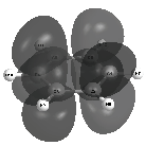
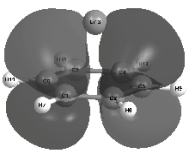
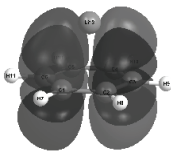
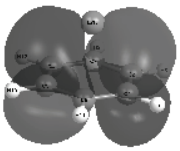
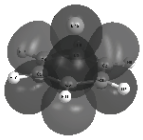
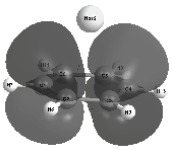
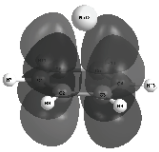
| System | $\lambda_{max}$ ($f$) | NTO | | | MO transitions, amplitude, contribution, % |
|---|---|---|---|---|---|
| | | Contribution, % | Hole | Particle | |
| B | 168.035 (0.559) | 50 |  |  | HOMO-1 → LUMO 0.69 (47%)<br>HOMO → LUMO+1 –0.69 (47%) |
| | | 50 |  |  | HOMO-1 → LUMO+1 –0.16 (2%)<br>HOMO → LUMO –0.16 (2%) |
| $Li^+$–B | 165.649 (0.522) | 49 |  |  | HOMO-1 → LUMO 0.62 (38%)<br>HOMO → LUMO+1 –0.62 (38%) |
| | | 49 |  |  | HOMO-1 → LUMO+1 0.33 (11%)<br>HOMO → LUMO 0.33 (11%) |
| $Na^+$–B | 168.357 (0.528) | 49 |  |  | HOMO-1 → LUMO+2 0.70 (49%)<br>HOMO → LUMO+1 –0.70 (49%) |

TABLE S-II. Continued

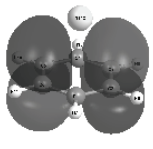
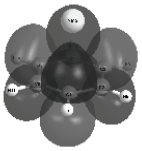
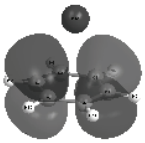
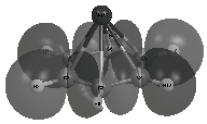
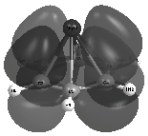
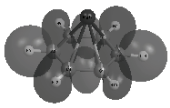
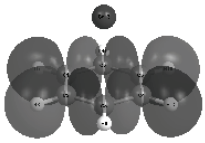
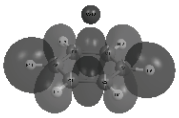
| System | $\lambda_{max}$ ($f$) | NTO | | | MO transitions, amplitude, contribution, % | | |
|---|---|---|---|---|---|---|---|
| | | Contribution, % | Hole | Particle | | | |
| $Na^+$–B | 168.357 (0.528) | 49 |  |  | | | |
| $K^+$–B | | 63 |  |  | HOMO-1 → LUMO+3 | 0.57 | (32%) |
| | | | | | HOMO → LUMO+1 | 0.57 | (32%) |
| | | | | | HOMO → LUMO+5 | 0.46 | (21%) |
| | 169.766 (0.344) | 34 |  |  | HOMO-1 → LUMO+5 | 0.28 | (8%) |
| | | | | | HOMO-1 → LUMO+1 | 0.15 | (2%) |
| $Mg^{2+}$– –B | 174.029 (0.011) | 53 |  |  | HOMO-2 → LUMO+1 | 0.73 | (53%) |
| | | | | | HOMO-3 → LUMO+2 | 0.67 | (45%) |
| | | 45 |  |  | | | |
| $Ca^{2+}$–B | 173.551 (0.007) | 49 |  |  | HOMO-3 → LUMO+2 | 0.70 | (49%) |
| | | | | | HOMO-2 → LUMO+1 | 0.70 | (48%) |
| | | 48 |  |  | | | |

TABLE S-III. NTO pictures and MO transitions corresponding to $\lambda_{max}$ / nm of the MBC systems under study

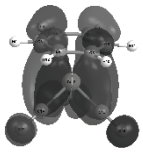
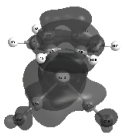
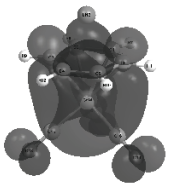
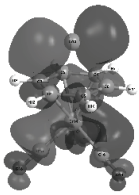
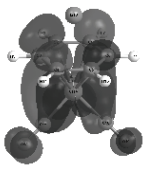
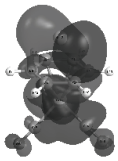
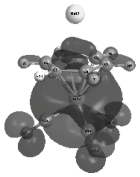
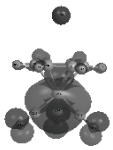
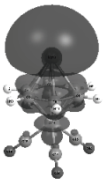
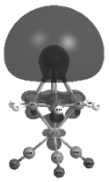
| System | $\lambda$max (*f*) | NTO Contri-bution, % | NTO Hole | NTO Particle | MO transitions, amplitude, contribution, % |
|---|---|---|---|---|---|
| BC | 328.925 (0.002) | 71 |  |  | HOMO-2 → LUMO+1 0.71 (51%)<br>HOMO-2 → LUMO+2 –0.37 (14%)<br>HOMO-1 → LUMO+3 0.28 (8%) |
| | | 10 |  |  | HOMO → LUMO+2 –0.27 (7%)<br>HOMO-2 → LUMO+13 –0.18 (3%)<br>HOMO-1 → LUMO+12 0.15 (2%) |
| $Li^+$–BC | 352.210 (0.003) | 49 |  |  | HOMO → LUMO+5 0.45 (21%)<br>HOMO → LUMO+4 –0.45 (20%)<br>HOMO-1 → LUMO+4 –0.44 (19%)<br>HOMO-1 → LUMO+5 –0.41 (17%) |
| | | 43 |  |  | HOMO → LUMO+12 –0.22 (5%)<br>HOMO-1 → LUMO+11 –0.20 (4%) |
| $Na^+$–BC | 351.840 (0.002) | 77 |  |  | HOMO-2 → LUMO+3 0.66 (43%)<br>HOMO-2 → LUMO+11 0.31 (10%)<br>HOMO-2 → LUMO+1 0.27 (7%)<br>HOMO-2 → LUMO+6 0.27 (7%)<br>HOMO → LUMO+4 0.23 (5%)<br>HOMO-1 → LUMO+3 0.23 (5%) |

TABLE S-III. Continued

| System | $\lambda_{max}$ (*f*) | NTO | | | MO transitions, amplitude, contribution, % | | |
|---|---|---|---|---|---|---|---|
| | | Contribution, % | Hole | Particle | | | |
| $K^+$–BC | 339.759 (0.001) | 70 |  |  | HOMO-3 → LUMO+2 | 0.56 | (31%) |
| | | | | | HOMO-3 → LUMO+1 | 0.39 | (15%) |
| | | | | | HOMO-3→ LUMO+5 | 0.39 | (15%) |
| | | | | | HOMO-3 → LUMO+14 | 0.21 | (4%) |
| | | | | | HOMO-2 → LUMO+3 | –0.20 | (4%) |
| | | | | | HOMO-2 → LUMO+2 | 0.17 | (3%) |
| $Mg^{2+}$– –BC | 792.337 (0.048) | 98 |  |  | HOMO-2 → LUMO | 0.99 | (98%) |
| $Ca^{2+}$— BC | 667.052 (0.017) | 99 |  |  | HOMO-2 → LUMO | 1.00 | (99%) |

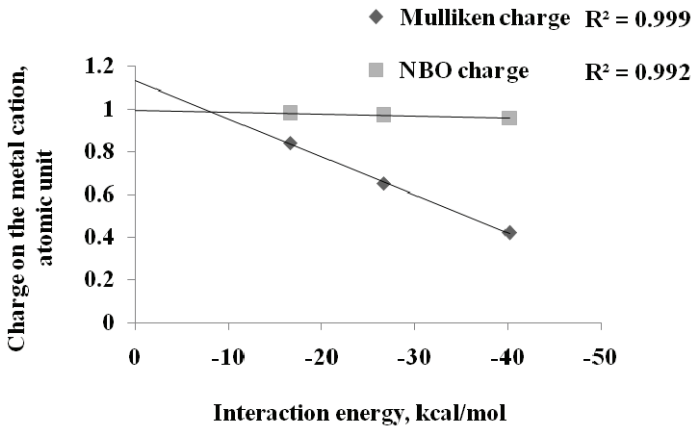



Fig. S-1. Interaction energy, kcal* $mol^{-1}$, *vs.* charge on the monovalent metal cations, atomic unit in the MB systems.

* 1 kcal = 4184 J

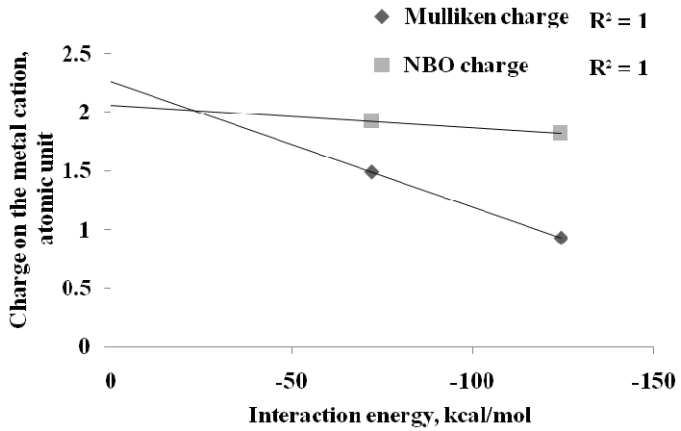



Fig. S-2. Interaction energy, kcal mol$^{-1}$, *vs.* charge on the divalent metal cations, atomic unit, in the MB systems.

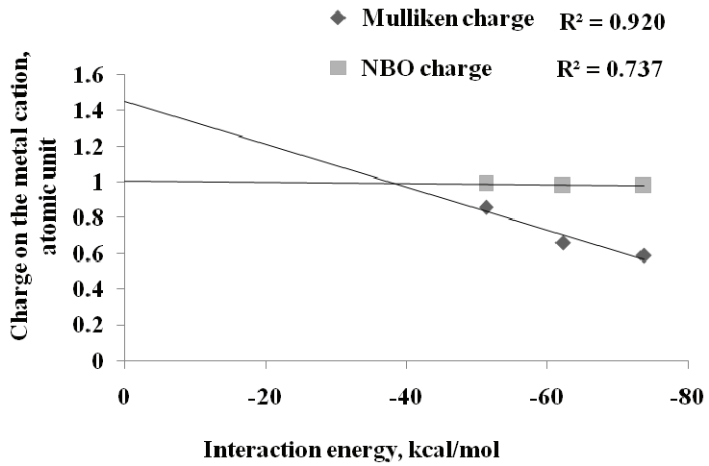



Fig. S-3. Interaction energy, kcal mol$^{-1}$, *vs.* charge on the monovalent metal cations, atomic unit, in the MBC systems.

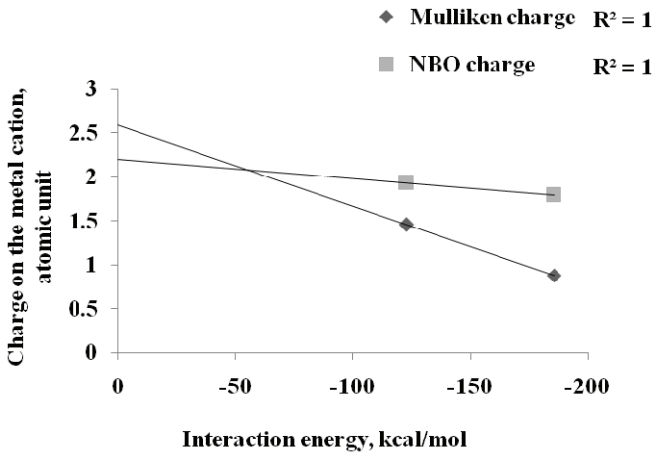



Fig. S-4. Interaction energy, kcal mol$^{-1}$, *vs.* charge on the divalent metal cations, atomic unit, in the MBC systems.

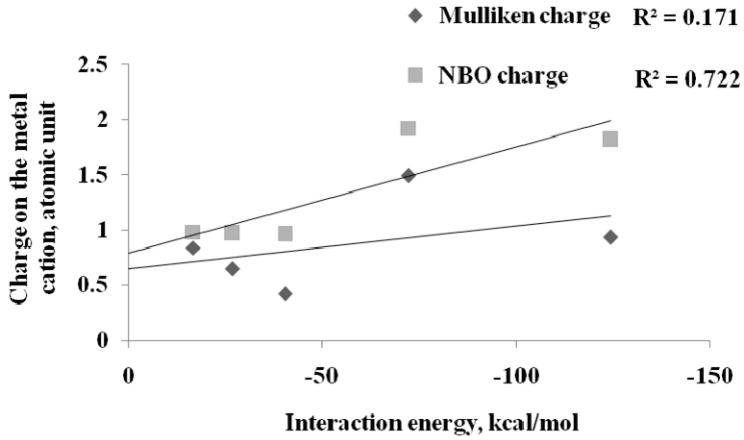



Fig. S-5. Interaction energy, kcal mol$^{-1}$, *vs*. charge on the metal cation, atomic unit, in the MB systems.

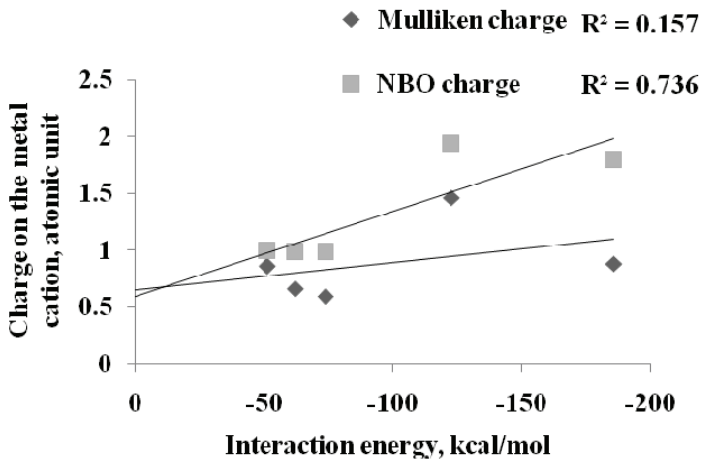



Fig. S-6. Interaction energy, kcal $mol^{-1}$, *vs.* charge on the metal cation, atomic unit, in the MBC systems.