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Supramolecular Structure of Tris(1,10-phenanthroline)zinc(II)-Cation and N,N0,N00-tris(carboxymethyl)-1,3,5-benzenetricarboxamide-Anion: Synthesis, Crystal Structure, Vibrational Spectra, and Theoretical Investigations

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Table S1. Selected bond lengths (Å) and bond angle (°) of the cationic complex.

Bond	Lengths	Bond	Lengths
Zn–N4	2.166 (4)	Zn–N7	2.163 (4)
Zn–N5	2.152 (4)	Zn–N8	2.183 (3)
Zn–N6	2.155 (3)	Zn–N9	2.180 (4)
Bond	**Angle**	**Bond**	**Angle**
N4–Zn–N5	77.50 (14)	N6–Zn–N5	98.94 (14)
N4–Zn–N6	101.77 (14)	N6–Zn–N7	77.32 (14)
N4–Zn–N7	94.87 (13)	N6–Zn–N8	166.80 (13)
N4–Zn–N8	90.05 (13)	N6–Zn–N9	92.02 (14)
N4–Zn–N9	165.01 (14)	N7–Zn–N8	96.00 (13)
N5–Zn–N7	170.76 (14)	N7–Zn–N9	93.87 (13)
N5–Zn–N8	89.28 (13)	N8–Zn–N9	76.93 (13)
N5–Zn–N9	94.71 (14)		

Table S2. Selected bond lengths (Å) and bond angle (°) of the dianion.

Bond	Lengths	Bond	Lengths
C1–C2	1.390 (6)	O3–C9	1.249 (5)
C1–C6	1.393 (6)	O4–C10	1.244 (5)
C1–C7	1.495 (6)	O5–C12	1.247 (6)
C2–C3	1.404 (6)	O6–C12	1.237 (6)
C3–C4	1.397 (6)	O7–C13	1.234 (5)
C3–C10	1.479 (6)	O8–C15	1.217 (6)
C4–C5	1.392 (6)	O9–C15	1.312 (6)
C5–C6	1.398 (6)	O9–H9	1.26 (10)
C5–C13	1.496 (6)	N1–C7	1.340 (6)
C8–C9	1.519 (6)	N1–C8	1.456 (5)
C11–C12	1.502 (6)	N2–C10	1.344 (5)
C14–C15	1.506 (6)	N2–C11	1.456 (5)
O1–C7	1.241 (5)	N3–C13	1.343 (5)
O2–C9	1.267 (5)	N3–C14	1.455 (5)
Bond	**Angle**	**Bond**	**Angle**

C2–C1–C6	119.6 (4)	O3–C9–C8	119.8 (4)
C2–C1–C7	122.0 (4)	O2–C9–C8	114.5 (4)
C6–C1–C7	118.4 (4)	O4–C10–N2	121.3 (4)
C1–C2–C3	121.3 (4)	O4–C10–C3	120.2 (4)
C4–C3–C2	118.2 (4)	N2–C10–C3	118.4 (4)
C4–C3–C10	124.2 (4)	N2–C11–C12	115.2 (4)
C2–C3–C10	117.5 (4)	O5–C12–O6	124.6 (5)
C3–C4–C5	120.9 (4)	O5–C12–C11	116.6 (4)
C6–C5–C4	119.9 (4)	O6–C12–C11	118.9 (4)
C6–C5–C13	120.5 (4)	O7–C13–N3	123.9 (4)
C4–C5–C13	119.6 (4)	O7–C13–C5	121.1 (4)
C5–C6–C1	119.9 (4)	N3–C13–C5	115.1 (4)
O1–C7–N1	123.3 (4)	N3–C14–C15	113.3 (4)
O1–C7–C1	119.7 (4)	O8–C15–O9	121.0 (5)
N1–C7–C1	117.0 (4)	O8–C15–C14	119.9 (4)
N1–C8–C9	114.9 (4)	O9–C15–C14	119.0 (4)
O3–C9–O2	125.6 (4)		

Tabel S3. Hydrogen-bond geometry (Å, °) for $[Zn(C_{12}H_8N_2)_3]C_{15}H_{13}N_3O_9\cdot 5H_2O$.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O10—H10*A*···O4	0.84 (3)	1.95 (3)	2.759 (5)	163 (6)
O10—H10*B*···O1^{i}	0.75 (6)	2.01 (6)	2.760 (5)	175 (7)
O11—H11*A*···O14	0.85 (7)	1.96 (7)	2.786 (6)	163 (7)
O11—H11*B*···O2^{i}	0.94 (7)	1.93 (7)	2.862 (5)	169 (6)
O12—H12*A*···O11^{ii}	0.98 (7)	1.86 (7)	2.831 (6)	166 (6)
O12—H12*B*···O13^{iii}	0.82 (7)	2.04 (7)	2.840 (6)	162 (7)
O13—H13*A*···O6^{iv}	0.87 (3)	2.55 (4)	3.394 (6)	163 (6)
O13—H13*B*···O2^{i}	0.99 (7)	1.78 (7)	2.773 (5)	176 (6)
O13—H13*B*···O3^{i}	0.99 (7)	2.56 (7)	3.202 (5)	122 (5)
O14—H14*C*···O10	0.89 (3)	1.86 (3)	2.734 (5)	167 (6)
O14—H14*D*···O8^{v}	0.86 (3)	2.00 (4)	2.769 (5)	148 (6)
N1—H1···O7^{v}	0.87	2.23	3.010 (5)	150
N2—H2···O3^{v}	0.87	2.07	2.873 (5)	153
N3—H3···O5^{vi}	0.87	1.93	2.753 (5)	158
O9—H9···O6^{vi}	1.22 (6)	1.35 (6)	2.544 (5)	165 (5)
C17—H17···O3^{i}	0.94	2.55	3.404 (6)	152
C29—H29···O3^{vii}	0.94	2.46	3.183 (6)	134
C29—H29···O6^{viii}	0.94	2.64	3.346 (7)	132
C37—H37···O11	0.94	2.49	3.144 (6)	127
C40—H40···O10	0.94	2.55	3.253 (6)	132
C40—H40···N4	0.94	2.67	3.221 (6)	118

Symmetry codes: (i) -*x*+1/2, *y*-1/2, *z*; (ii) -*x*+1, *y*+1/2, -*z*+1/2; (iii) -*x*+3/2, *y*+1/2, *z*; (iv) *x*+1/2, -*y*+1/2, -*z*+1; (v) -*x*, -*y*+1, -*z*+1; (vi) -*x*+1/2, *y*+1/2, *z*; (vii) *x*+1, *y*, *z*; (viii) -*x*+1, -*y*+1, -*z*+1.

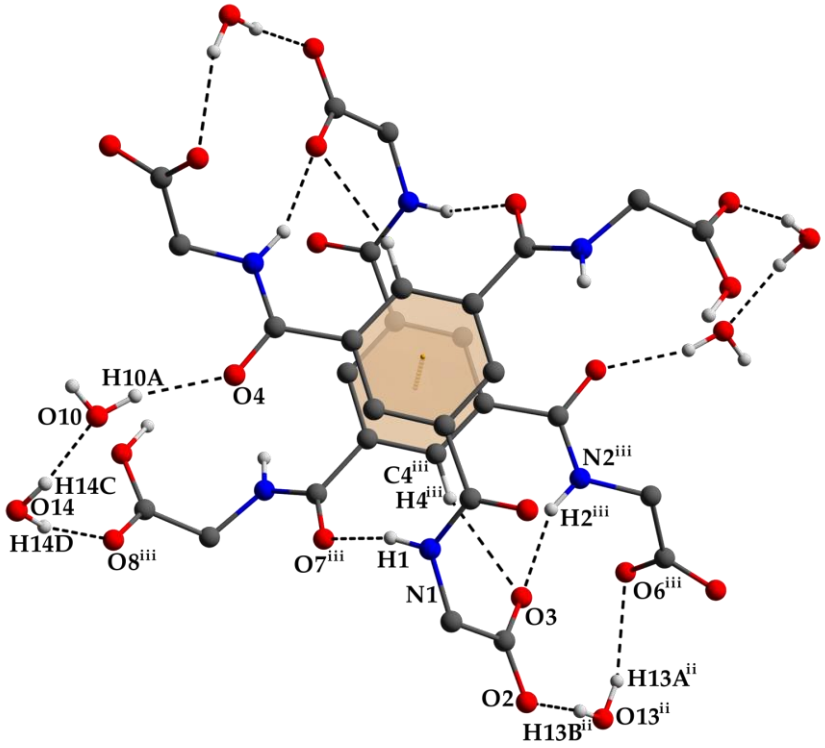

Figure S1. View of the dimeric anions with hydrogen bonds (black dashed lines) and π–π-interaction (yellow dashed lines). The carbon–hydrogen atoms have been omitted for clarity. Symmetry codes: (ii) -x+1/2, y+1/2, z; (iii) -x, -y+1, -z+1.

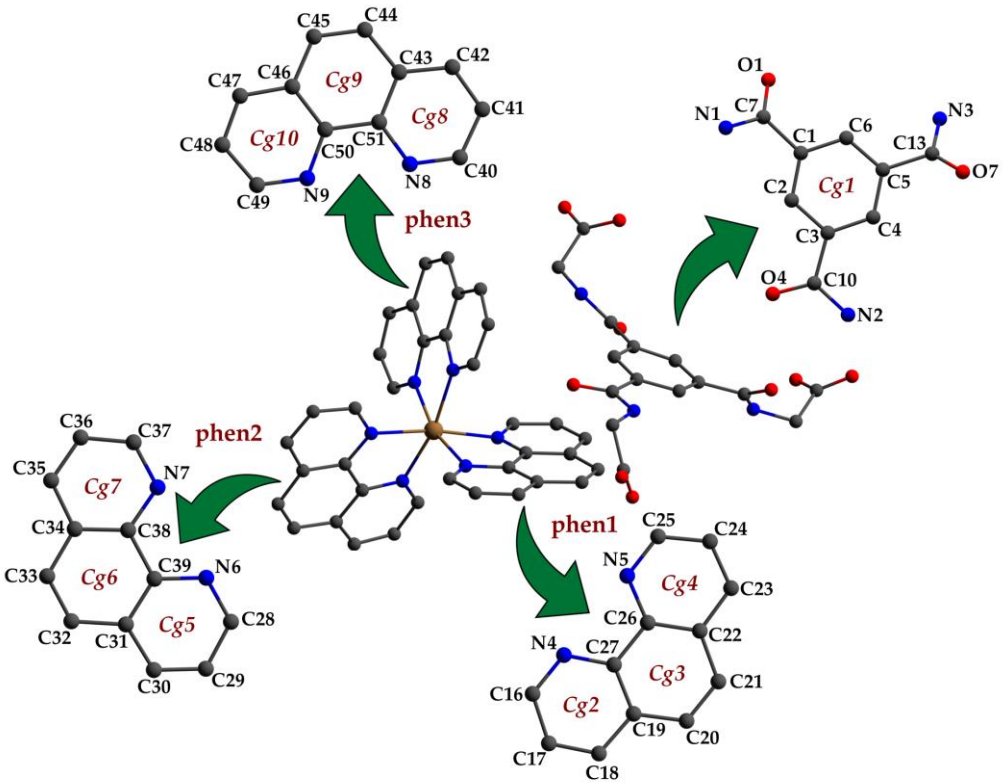

Figure S2. Defintion of centroids of the phenantrholines of the cationic complex and the dianion with numbering, respectively. The hydrogen atoms have been omitted for clarity.

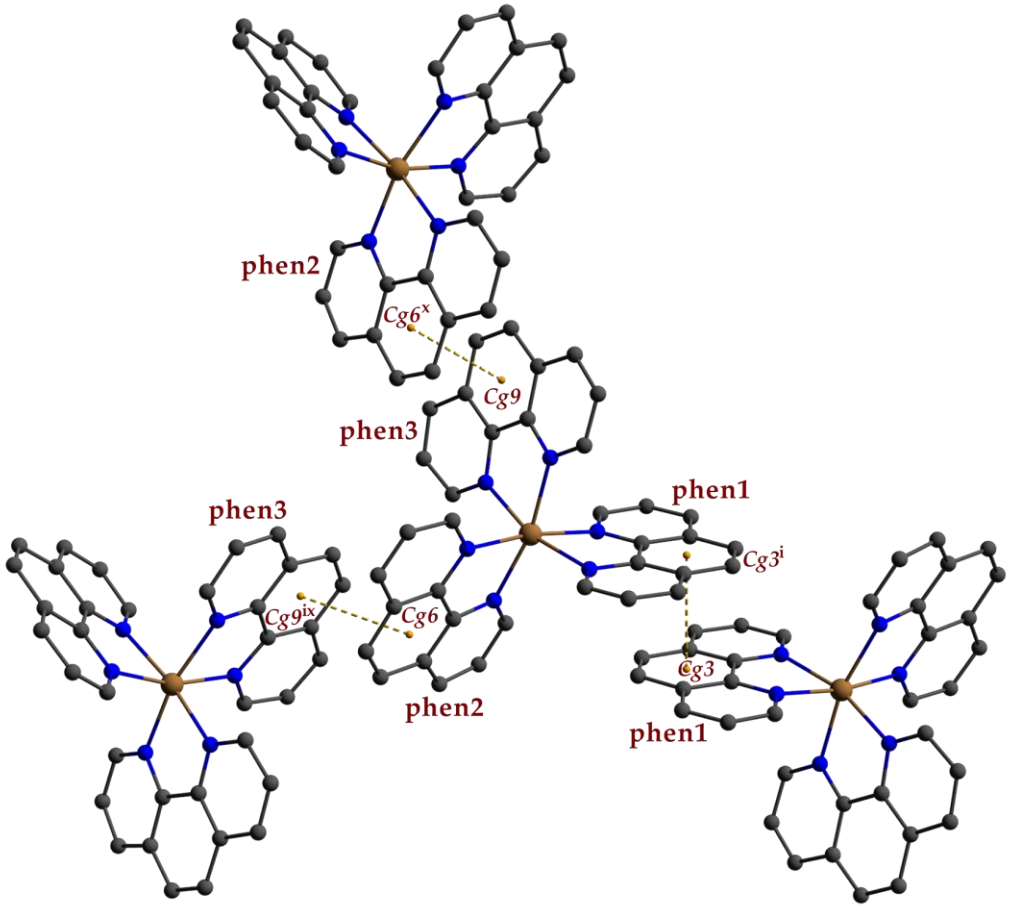

Figure S3. View of the three-dimensional cationic π–π-interactions (yellow dashed lines). The hydrogen atoms have been omitted for clarity. Symmetry codes: (i) -x+1, -y+1, -z+1; (ix) x+1/2, y, -z+1/2; (x) x-1/2, y, -z+1/2.

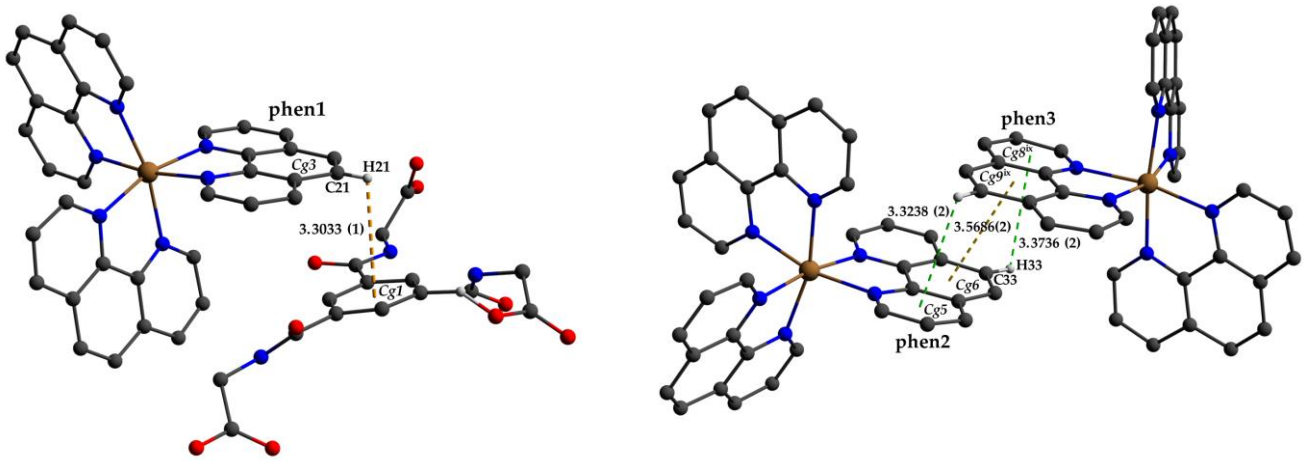

Figure S4. Representation of the C–H···π interaction of the phenanthroline 1 and the dianion (left) as well as the π-stacking and C–H···π interactions of the phenanthroline 2 and 3 (right). The hydrogen atoms have been omitted for clarity. Bond lengths are given in Å. Symmetry code: (ix) x+1/2, y, -z+1/2.

Tabel S4. Pairwise interaction energies (kJ/mol) calculated with PSI4 (SAPT0).

Pairs	Basis set	
	jun-cc-pVDZ	**aug-cc-pVDZ**
dimeric anions		
Electrostatics	401.44	407.80
Exchange	124.47	124.79
Induction	-83.61	-87.06
Dispersion	-108.72	-128.12
Total SAPT0	333.58	317.41
phen1 – phen1		
Electrostatics	-24.46	-24.06
Exchange	49.23	49.50
Induction	-5.75	-5.88
Dispersion	-72.425	-82.70
Total SAPT0	-53.40	-63.13
phen2 – phen3		
Electrostatics	-29.17	-29.01
Exchange	55.77	56.12
Induction	-6.59	-6.80
Dispersion	-67.73	-77.49
Total SAPT0	-47.72	-57.17
phen1 – dianion		
Electrostatics	-37.09	-36.52
Exchange	39.64	39.67
Induction	-16.28	-16.92
Dispersion	-53.70	-62.91
Total SAPT0	-67.43	-76.69
phen3 – dianion		
Electrostatics	-13.08	-12.53
Exchange	15.47	15.48
Induction	-8.28	-8.70
Dispersion	-24.00	-28.25
Total SAPT0	-29.89	-33.99

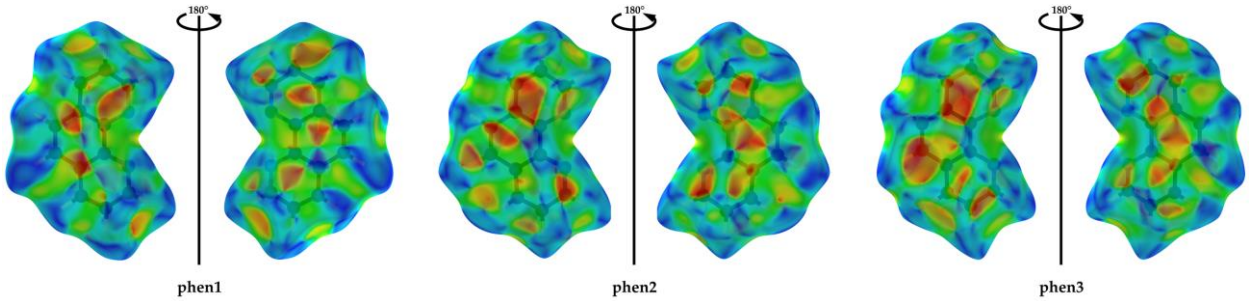

Figure S5. Graphical representations of the Hirshfeld surfaces of the phenanthrolin ligands of the cationic complex drawn with transparency and mapped over the shape index.

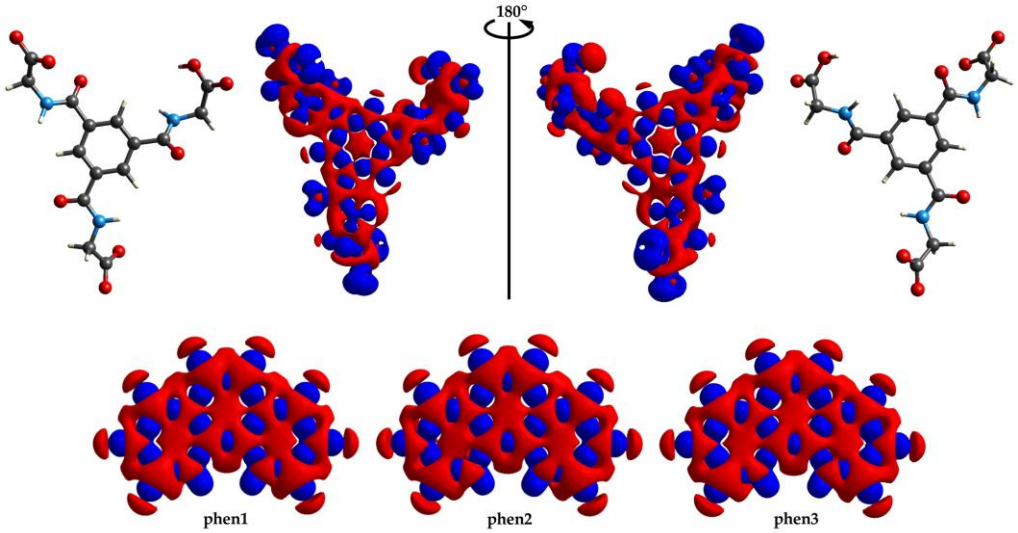

Figure S6. Graphical representations of the Hirshfeld surfaces of the dianion (upper part) and the phenanthrolin ligands of the cationic complex (lower part) mapped over the deformation density.

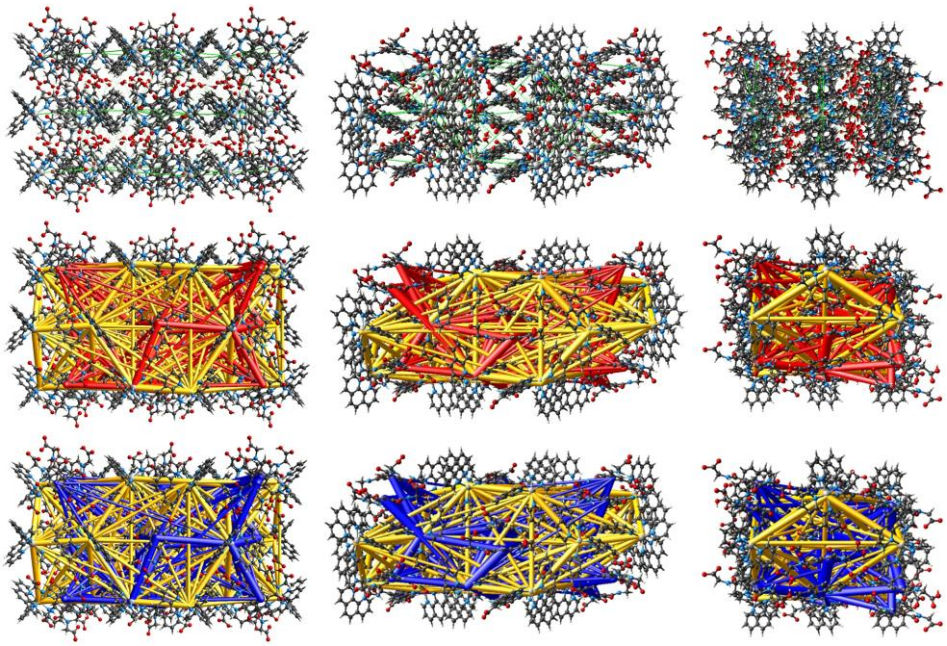

Figure S7. Visualization of the energy framework in the crystal along the *a* axis (left), *b* axis (middle), and *c* axis (right) of the dispersion energy (top), the coulomb energy (middle), and the total energy (bottom).

Table S5. Pairwise interaction energies of the cationic complexes and anions with color code. Interaction Energy is given in kJ/mol and R is the distance between molecular centroids (mean atomic position) in Å.

Anions

N	Symop	R	Electron Density	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
1	-x, -y, -z	3.47	B3LYP/6-31G(d,p)	644.29	-100.70	-83.41	124.41	610.91
1	-x, -y, -z	3.47	B3LYP/DGDZVP	606.40	-101.10	-83.41	158.62	591.69
1	-x, -y, -z	3.47	HF/3-21G	627.37	-115.35	-83.41	89.08	561.26
2	-x+1/2, y+1/2, z	10.91	B3LYP/6-31G(d,p)	290.15	-125.16	-20.84	156.94	292.95
2	-x+1/2, y+1/2, z	10.91	B3LYP/DGDZVP	268.82	-123.22	-20.84	187.67	290.83
2	-x+1/2, y+1/2, z	10.91	HF/3-21G	265.86	-149.09	-20.84	119.03	251.63

Cationic complexes

N	Symop	R	Electron Density	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
2	x+1/2, y, -z+1/2	10.02	B3LYP/6-31G(d,p)	541.58	-59.19	-74.24	46.82	493.09
2	x+1/2, y, -z+1/2	10.02	B3LYP/DGDZVP	525.27	-58.36	-74.24	71.84	491.91
2	x+1/2, y, -z+1/2	10.02	HF/3-21G	537.49	-55.41	-74.24	38.27	475.73
1	-x, -y, -z	9.40	B3LYP/6-31G(d,p)	551.28	-61.32	-77.71	41.31	495.35
1	-x, -y, -z	9.40	B3LYP/DGDZVP	537.27	-60.48	-77.71	63.49	494.86
1	-x, -y, -z	9.40	HF/3-21G	544.00	-55.86	-77.71	34.10	475.56

Cation – Anion

N	Symop	R	Electron Density	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
1	-	7.43	B3LYP/6-31G(d,p)	-649.16	-64.74	-68.88	38.50	-770.45
1	-	7.43	B3LYP/DGDZVP	-659.32	-63.50	-68.88	58.60	-767.86
1	-	7.43	HF/3-21G	-639.86	-59.80	-68.88	30.34	-728.32

Scale factors for benchmarked energy models [1]

Energy Model	k_{ele}	k_{pol}	k_{disp}	k_{rep}
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see [59]).